Exam Review Packet – Student Version

Table of Contents

Directions

Multiple Choice Section

In section 1, there are 60 multiple choice questions . These questions represent the knowledge and skills students should know, understand, and be able to apply and students have 90 minutes to play. Students will be given a periodic table and an equations and constants list to use during this section.

For all questions, assume that the temperature is 298 K, the pressure is 1.00 atmosphere, and solutions are aqueous unless otherwise specified.

Free Response section

Section II Directions: Questions 1 through 3 are long constructed response questions that should require about 20 minutes each to answer. Questions 4 through 7 are short constructed response questions that should require about 7 minutes each to answer. Students have 105 minutes for this setionRead each question carefully and write your response in the space provided following each question. Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Specific answers are preferable to broad, diffuse responses. For calculations, clearly show the method used and the steps involved in arriving at your answers. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not.

Periodic Table and Equations / Constants Sheet

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL	= liter(s), milliliter(s)	mm Hg	= millimeters of mercury
g	= gram(s)	J, kJ	= joule(s), kilojoule(s)
nm	= nanometer(s)	V	= volt(s)
atm	= atmosphere(s)	mol	= mole(s)

ATOMIC STRUCTURE

$E = h\nu$

$c = \lambda\nu$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^{8}$ m s^{-1}

Avogadro's number = 6.022×10^{23} mol^{-1}

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \text{ where } a\,A + b\,B \rightleftarrows c\,C + d\,D$$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ C$$

$$= K_a \times K_b$$

$$pH = -\log[H^+],\ pOH = -\log[OH^-]$$

$$14 = pH + pOH$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a,\ pK_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{total} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{total} = P_A + P_B + P_C + \ldots$$

$$n = \frac{m}{M}$$

$$K = °C + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure
V = volume
T = temperature
n = number of moles
m = mass
M = molar mass
D = density
KE = kinetic energy
v = velocity
A = absorbance
a = molar absorptivity
b = path length
c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$
$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$
1 atm = 760 mm Hg
= 760 torr
STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S° = \sum S° \text{ products} - \sum S° \text{ reactants}$$

$$\Delta H° = \sum \Delta H_f° \text{ products} - \sum \Delta H_f° \text{ reactants}$$

$$\Delta G° = \sum \Delta G_f° \text{ products} - \sum \Delta G_f° \text{ reactants}$$

$$\Delta G° = \Delta H° - T\Delta S°$$

$$= -RT \ln K$$

$$= -nFE°$$

$$I = \frac{q}{t}$$

q = heat
m = mass
c = specific heat capacity
T = temperature
$S°$ = standard entropy
$H°$ = standard enthalpy
$G°$ = standard free energy
n = number of moles
$E°$ = standard reduction potential
I = current (amperes)
q = charge (coulombs)
t = time (seconds)

Faraday's constant, F = 96,485 coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

DO NOT DETACH FROM BOOK.

PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.91	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 ***La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.02	89 **†Ac** 227.03	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)							

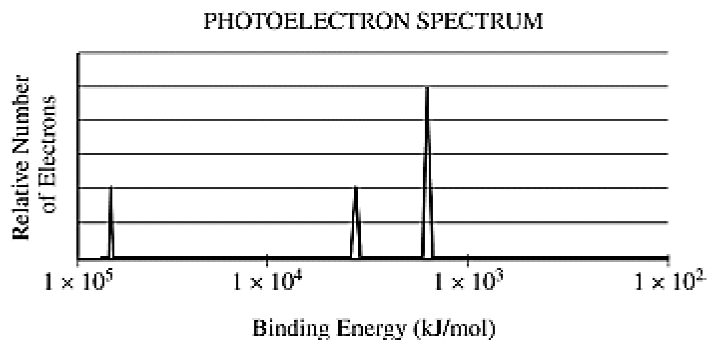
*Lanthanide Series	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
†Actinide Series	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Big Idea 1: The chemical elements are fundamental building materials of matter, and all matter can be understood in terms of arrangement of atoms. These atoms retain their identity in chemical reactions

Free Response Questions

1-1. Use the details of modern atomic theory to explain each of the following experimental observations.

a. Within a family such as the alkali metals, the ionic radius increases as the atomic number increases.
b. The radius of the chlorine atom is smaller than the radius of the chloride ion, Cl^{-}. (Radii: Cl atom = 0.99 Å; Cl= ion = 1.81 Å)
c. The first ionization energy of aluminum is lower than the first ionization energy of magnesium. (First ionization energies: $_{12}$Mg = 7.6 ev, $_{13}$Al = 6.0 ev)
d. For magnesium, the difference between the second and third ionization energies is much larger than the difference between the first and second ionization energies. (Ionization energies, in electron-volts, for Mg: 1st = 7.6, 2nd = 14, 3rd = 80)



Peak 1	Peak 2	Peak 3
6.72×10^4 kJ/mol	3.88×10^3 kJ/mol	1.68×10^3 kJ/mol

1-2. The complete photoelectron spectrum of an unknown element is shown above. The frequency ranges of different regions of the electromagnetic spectrum are given in the table below.

Region of Electromagnetic Spectrum	Frequency Range (s^{-1})
Infrared (IR)	1×10^{12} to 4×10^{14}
Ultraviolet/visible (UV/vis)	4×10^{14} to 5×10^{16}
X-rays	5×10^{16} to 1×10^{19}
Gamma rays	$> 1 \times 10^{19}$

(a) To generate the spectrum above, a source capable of producing electromagnetic radiation with an energy of 7 x 10^4 kJ per mole of photons was used. Such radiation is from which region of the electromagnetic spectrum? Justify your answer with a calculation.

(b) A student examines the spectrum and proposes that the second ionization energy of the element is 2.88 x 103kJ/mol. To refute the proposed interpretation of the spectrum, identify the following/
(i) The subshell from which an electron is removed in the second ionization of an atom of the element
(ii) The subshell that corresponds to the second peak of the photoelectron spectrum above

1-3. Answer the following questions relating to the elements gallium and arsenic

(a) Write the ground-state electron configuration for an atom of each of the following.

(i) Ga

(ii) As

	Ionization Energy	
	First	Second
Gallium	580	1980
Arsenic	950	1800

(b) Consider the information in the table on the left.

(i) Explain, in terms of atomic structure, why As has a higher first ionization energy than Ga.

(ii) Explain, in terms of atomic structure, why Ga has a higher second ionization energy than As.

(c) Consider the Ga+ ion.

(i) Identify an ion of As that is isoelectronic with Ga+.

(ii) Which species has a larger radius: Ga^{+} or the ion you identified in part (c)(i)? Explain.

(d) Arsenic reacts with fluorine to form AsF5.

(i) Draw the complete Lewis electron-dot diagram for the AsF5 molecule.

(ii) Are all of the F-As-F bond angles in the AsF5 molecule the same? Explain

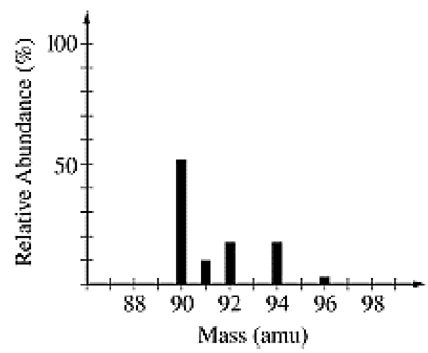
Multiple Choice

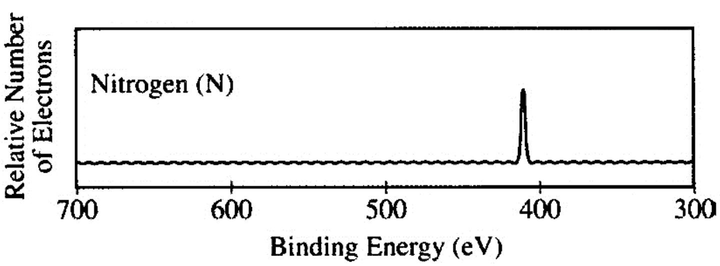
1-4 Which of the following elements has the largest first ionization energy?

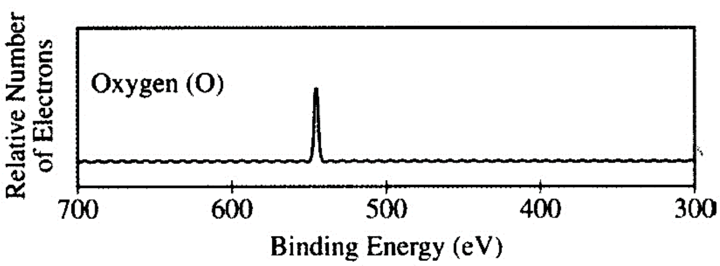
a. Li b. Be c. B d. C e. N

1-5. The mass spectrum of element X is presented in the diagram at the right. Based on the spectrum, which of the following can be concluded about element X?

a. X is a transition metal, and each peak represents an oxidation state of the metal.
b. X contains five electron sublevels
c. The atomic mass of X is 90.
d. The atomic mass of X is between 90 and 92.





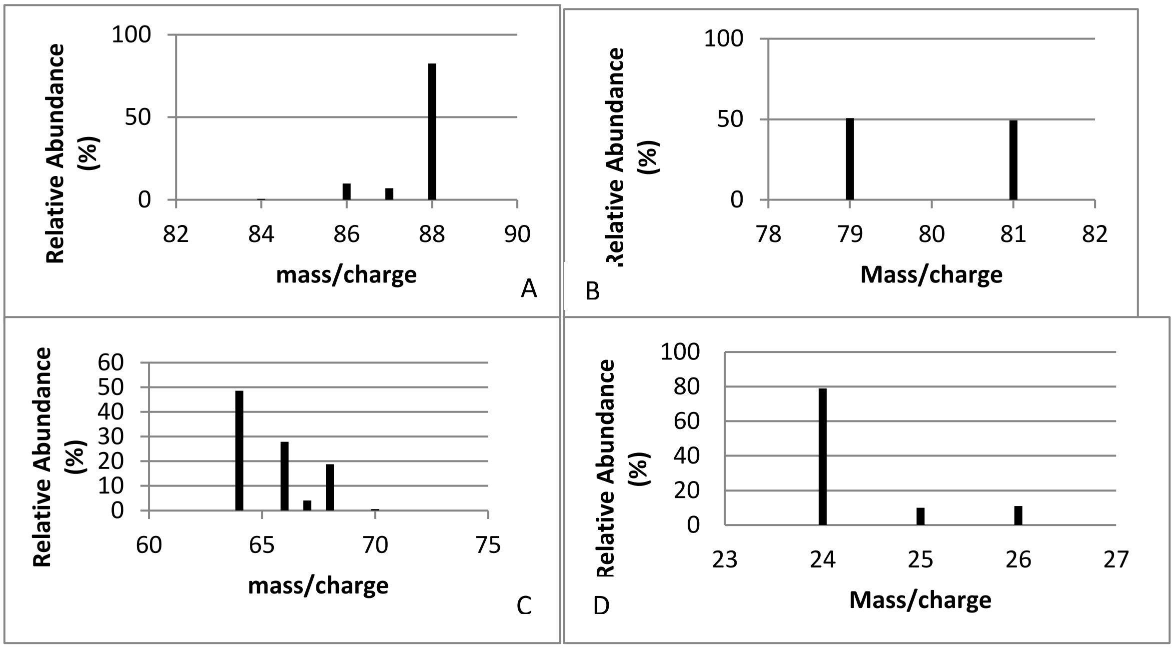


1-6. The photoelectron spectra show the energy required to remove a 1s electron from a nitrogen atom and from an oxygen atom. Which of the following statements best accounts for the peak in the upper spectrum being to the right of the peak in the lower spectrum?

a. Nitrogen atoms have a half-filled p subshell.
b. There are more electron-electron repulsions in oxygen atoms than ibn nitrogen atoms.
c. Electrons in the p subshell of oxygen atoms providing more shielding than electrons in the p subshell of nitrogen atoms.
d. Nitrogen atoms have a smaller nuclear charge than oxygen atoms.

1-7. Which of the following is the electron configuration of an excited atom that is likely to emit a quantum of energy?

a. $1s^2\ 2s^2 2p^6\ 3s^2 3p^1$ b. $1s^2\ 2s^2 2p^6\ 3s^2 3p^5$ c. $1s^2\ 2s^2 2p^6\ 3s^2$ d. $1s^2\ 2s^2 2p^6\ 3s^1$ e. $1s^2\ 2s^2 2p^6\ 3s^1 3p^1$



Mass spectrums of 4 different elements are presented above and apply to question 1-8 to 1-10

1-8. Which spectrum shows the isotopes of Zn? A B C D

1-9. Which value is closest to the average atomic mass of Element B? (A) 79 (B) 80 (C) 81 (D)160

1-10. Which element has the highest ionization energy? A B C D

1-11. Which of the following lists Mg, P, and Cl in order of increasing atomic radius?

a. Cl < P < Mg b. Cl < Mg < P c. Mg < P < Cl d. Mg < Cl < P

1-12. Which of the following correctly identifies which has the higher first ionization energy, Cl or Ar, and supplies the best justification?

a. Cl, because of its higher electronegativity

b. Cl, because of its higher electron affinity

c. Ar, because of its completely filled valence shell

d. Ar, because of its higher effective nuclear charge

1-13. To gravimetrically analyze the silver content of a piece of jewelry made from an alloy of Ag and Cu, a student dissolves a small preweighed sample in HNO_3(aq). Ag^+(aq) and Cu^{2+} (aq) ions form in the solution. Which of the following should be the next step in the analytical process?

a. Centrifuging the solution to isolate the heavier ions.

b. Evaporating the solution to recover the dissolved nitrates.

c. Adding enough bas solution to bring the pH up to 7.0.

d. Adding a solution containing an anion that forms an insoluble salt with only one of the metal ions.

Big Idea 2: Chemical and physical properties of materials can be explained by the structure and arrangement of atoms, ions, or molecules and the forces between them

Free Response Questions

Molecule	Boiling Point of Compound (K)	Dipole Moment (debyes)	Polarizability (10^{-24} cm^3)
HCl	188	1.05	2.63
HBr	207	0.80	3.61
HI	238	0.38	5.44

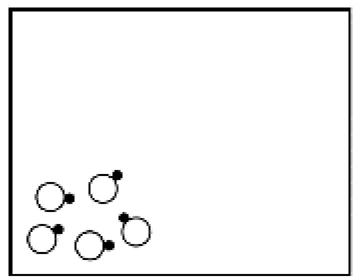
2-1. The boiling points, dipole moments, and polarizabilities of three hydrogen halides are given in the table above.

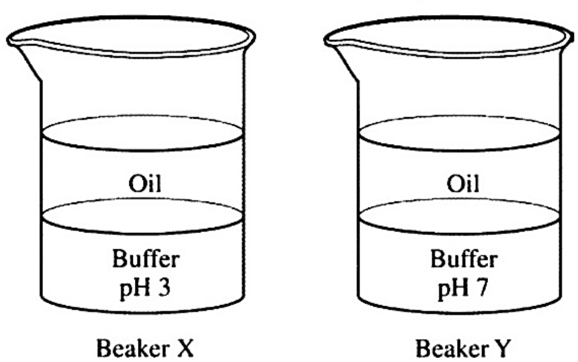
a. Based on the data in the table, what type of intermolecular force among the molecules HCl(*l*), HBr(*l*), and HI(*l*) is able to account for the trend in boiling points? Justify your answer.

b. Based on the data in the table, a student predicts that the boiling point of HF should be 174 K. The observed boiling point of HF is 293K. Explain the failure of the student's prediction in terms of the types and strengths of the intermolecular forces that exist among HF molecules.

c. A representation of five molecules of HBr in the liquid state is shown in the box on the right. Draw a representation of the 5 molecules of HBr after complete vaporization has occurred.

d. Draw a second representation of the 5 molecules at a temperature that is 100 K higher than the first box you drew.





2-2.

$$HIn(aq) + H_2O(l) \rightarrow In^-(aq) + H_3O^+(aq)$$

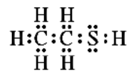
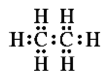
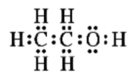
Yellow blue

The indicator HIn is a weak acid with a pK_a value of 5.0. It reacts with water as represented in the equation above. Consider the two beakers below. Each beaker has a layer of colorless oil (a nonpolar solvent) on top of a layer of aqueous buffer solution. In beaker X the pH of the buffer solution is 3, and in beaker Y the pH of the buffer solution is 7. A small amount of HIn is placed in both beakers. The mixtures are stirred well, and the oil and water layers are allowed to separate.

a. What is the predominant form of HIn in the aqueous buffer in beaker Y, the acid form or the conjugate base form? Explain your reasoning.

b. In beaker X the oil layer is yellow, whereas in beaker Y the oil layer is colorless. Explain these observations in terms of both acid-base equilibria and interparticle forces.

2-3 Use the information in the table below to respond to the statements and questions that follow. Your answers should be in terms of principles of molecular structure and intermolecular forces.

Compound	Formula	Lewis Electron-Dot Diagram
Ethanethiol	CH_3CH_2SH	
Ethane	CH_3CH_3	
Ethanol	CH_3CH_2OH	
Ethyne	C_2H_2	

a. Draw the complete Lewis electron dot diagram for ethyne in the appropriate cell in the table above.

b. Which of the four molecules contains the shortest carbon-carbon bond? Explain.

c. A Lewis electron dot diagram of a molecule of ethanoic acid is given below. The carbon atoms in the molecule are labeled *x* and *y*, respectively. Identify the geometry of the arrangement of atoms bonded to each of the following.

i. Carbon *x*

ii. Carbon *y*

d. In the molecule, the angle around C *x* is not 90°. Estimate the angle and explain in terms of electron pair geometry (VSPER)

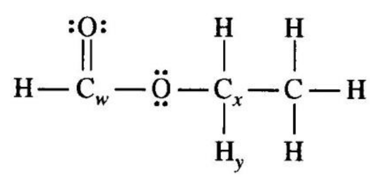
e. Energy is required to boil ethanol. Consider the statement "As ethanol boils, energy goes into breaking C-C bonds, C-H bonds, C-O bonds, and O-H bonds." Is the statement true or false? Justify your answer.

f. Identify a compound from the table above that is nonpolar. Justify your answer.

g. Ethanol is completely soluble in water, whereas ethanethiol has limited solubility in water. Account for the difference in solubilities between the two compounds in terms of intermolecular forces.

2-4 Use principles of molecular structure, intermolecular forces, and kinetic molecular theory to answer the following questions.

a. A complete Lewis electron dot diagram of a molecule of ethyl methanoate is shown to the right.



i. Identify the hybridization of the valence electrons of the carbon atoms labeled C_w.

ii. Estimate the numerical value of the $H_y - C_x - O$ bond angle in an ethyl methanoate molecule. Explain the basis of your estimate.

b. Ethyl methanoate, CH_3CH_2OCHO, is synthesized in the laboratory from ethanol, C_2H_5OH, and methanoic acid, $HCOOH$, as represented by the following equation.

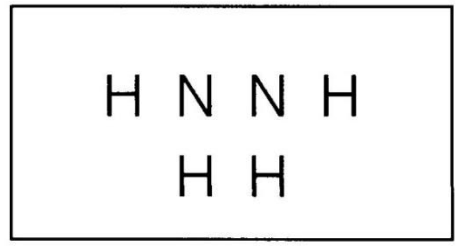
$$C_2H_5OH(l) + HCOOH(l) \rightarrow CH_3CH_2OCHO(l) + H_2O(l)$$

i. Draw the complete Lewis electron dot diagram of a methanoic acid molecule.

ii. Draw the complete Lewis electron dot diagrams of a methanoic acid molecule and a water molecule in an orientation that allows a hydrogen bond to form between them.

2-5 Hydrazine is an inorganic compound with the formula N_2H_4.

a. Complete the Lewis electron-dot diagram for the N_2H_4 molecule by drawing in all the electron pairs.



b. On the basis of the diagram you complete in part (a), do all six atoms in the N_2H_4 molecule lie in the same plane? Explain.

c. The normal boiling point of N_2H_4 is 114 ^oC, whereas the normal boiling point of C_2H_6 is -89 ^oC. Explain, in terms of the intermolecular forces present in <u>each</u> liquid, which the boiling point of N_2H_4 is so much higher than that of C_2H_6.

d. Write a balanced chemical equation for the reaction between N_2H_4 and H_2O that explains why a solution of hydrazine in water has a pH greater than 7.

N_2H_4 reacts in air according to the equation below.

$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(g) \qquad \Delta H^o = -534\ kJ\ mol^{-1}$

e. Is the reaction an oxidation-reduction, acid-base, or decomposition reaction? Justify your answer.

Multiple Choice Questions

2-6 The lattice energy of a salt is related to the energy required to separate the ions. For which of the following pairs of ions is the energy that is required to separate the ions largest? (Assume that the distance between the ions in each pair is equal to the sum of the ionic radii.)

a. $Na^+(g)$ and $Cl^-(g)$ b. $Cs^+(g)$ and $Br^-(g)$ c. $Mg^{2+}(g)$ and $O^{2-}(g)$ d. $Ca^{2+}(g)$ and $O^{2-}(g)$

Questions 2-7 through 2-10 refer to the following species: a. H_2O b. NH_3 c. BH_3 d. CH_4

2-7. Has two lone pairs of electrons

2-8. Has a central atom with less than an octet of electrons

2-9. Is predicted to have the largest bond angle

2-10. Has a trigonal-pyramidal molecular geometry

2-11. Which of the following lists the substances F_2, HCl, and HF in order of increasing boiling point?

a. $HF < HCl < F_2$ b. $HF < F_2 < HCl$ c. $HCl < F_2 < HF$ d. $F_2 < HCl < HF$

2-12. Which of the following is an isomer of CH_3OCH_3?

a. CH_3CH_3 b. CH_3COOH c. CH_3CH_2OH d.$CH_3CH_2CH_3$ e.$CH_3CH_2OCH_2CH_3$

2-13. Which of the following substances has the greatest solubility in $C_5H_{12}(l)$ at 1 atm?

a. $SiO_2(s)$ b. $NaCl(s)$ c. $H_2O(l)$ d. $CCl_4(l)$ e. $NH_3(g)$

2-14. Which of the following molecules contains exactly three sigma (σ) bonds and two pi (π) bonds?

a. C_2H_2 b. CO_2 c. HCN d. SO_3 e. N_2

2-15. Resonance is most commonly used to describe the bonding in molecules of which of the following?

a. CO_2 b. O_3 c. H_2O d. CH_4 e. SF_6

2-16. High solubility of an ionic solid in water is favored by which of the following conditions?

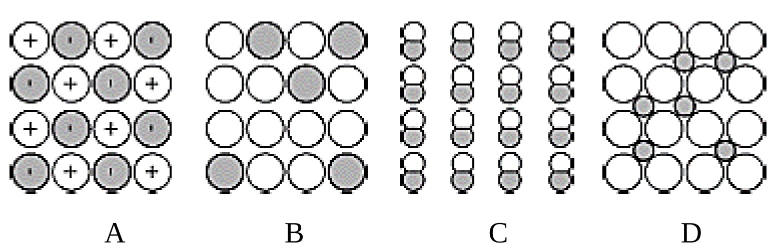
I. The existence of strong ionic attractions in the crystal lattice

II. The formation of strong ion-dipole attractions

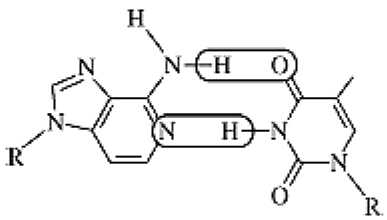
III. An increase in entropy upon dissolving

a. I only b. I and II only c.I and III only d.II and III only e. I, II, and III

2-17. Which of the following diagrams best depicts an alloy of Ni and B?

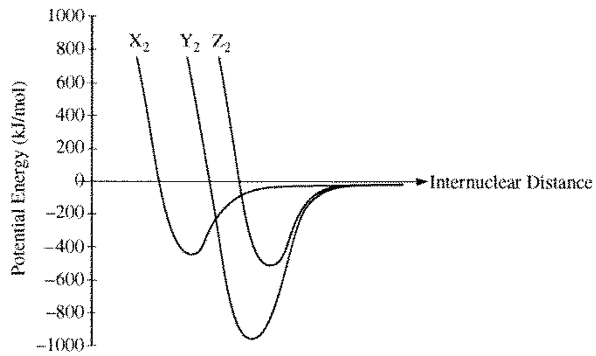


2-18



Which of the following is the strongest type of interaction that occurs between the atoms within the circled areas of the two molecules represented on the left?

a. Polar covalent bond b. nonpolar covalent bond
c. Hydrogen bond d. London dispersion forces

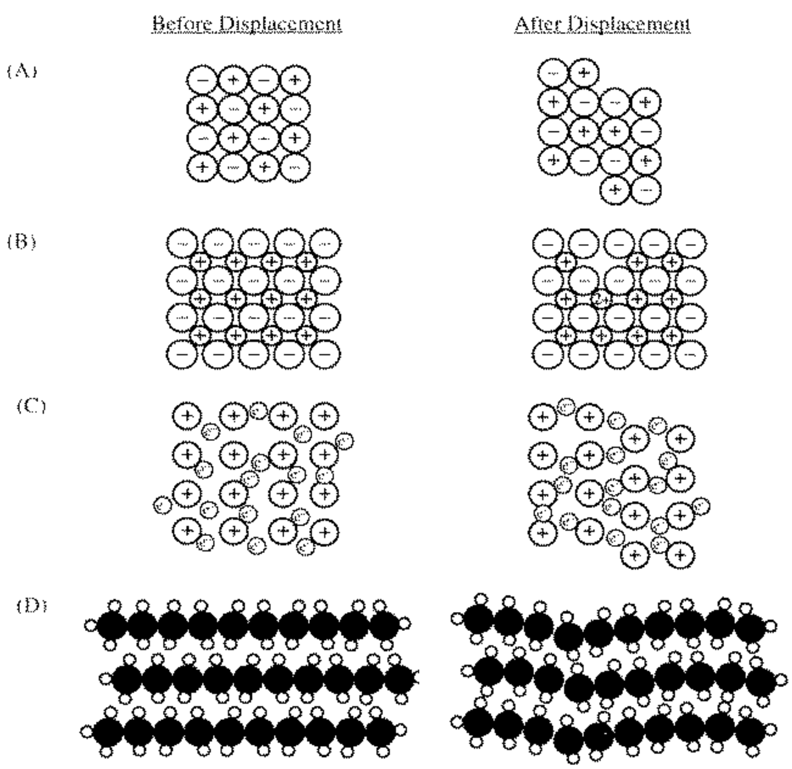


2-19.

The potential energy as a function of internuclear distance for three diatomic molecules, X_2, Y_2, and Z_2, is shown in the graph above. Based on the data in the graph, which of the following correctly identifies the diatomic molecules, X_2, Y_2, and Z_2?

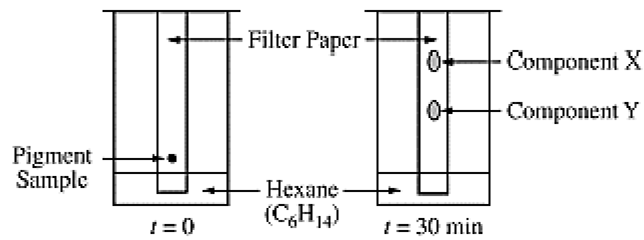
	X_2	Y_2	Z_2
a.	H_2	N_2	O_2
b.	H_2	O_2	N_2
c.	N_2	O_2	H_2
d.	O_2	H_2	N_2

2-20 Which of the following diagrams best illustrates how a displacement in an ionic crystal results in cleavage and brittleness?



2-21. In a paper chromatography experiment, a sample of a pigment is separated into two components, X and Y, as shown on the right. The surface of the paper is moderately polar. What can be concluded about X and Y based on the experimental results?

a. X has a larger molar mass than Y does.
b. Y has a larger molar mass than X does.
c. X is more polar than Y.
d. Y is more polar than X.



Element	Metallic radius (pm)	Melting point (°C)	Common oxidation state
Au	144	1064	1+ 3+
Cu	128	1085	1+ 2+
Ag	144	961	1+

2-22 To make Au stronger and harder, it is often alloyed with other metals, such as Cu and Ag. Consider two alloys, one of Au and Cu and one of Au and Ag, each with the same mole fraction of Au. If the Au/Cu alloy is harder than the Au/Ag alloy, then which of the following is the best explanation based on the information in the table above?

a. Cu has two common oxidation states, but Ag has only one.
b. Cu has a higher melting point than Au has, but Ag has a lower melting point than Au has.
c. Cu atoms are smaller than Ag atoms, thus they interfere more with the displacement of atoms in the alloy.
d. Cu atoms are less polarizable than are Au or Ag atoms, thus Cu has weaker interparticle forces.

Big Idea 3: Changes in matter involve the rearrangement and / or reorganization of atoms and / or the transfer of electrons

Free Response Questions

3-1 $Mg(s) + 2\ H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

A student performs an experiment to determine the volume of hydrogen gas produced when a given mass of magnesium reacts with excess HCl(aq), as represented by the net ionic equation above. The student begins with a 0.0360 g sample of pure magnesium and a solution of 2.0 M HCl(aq).

a. Calculate the number of moles of magnesium in the 0.0360 g sample.

b. Calculate the number of moles of HCl(aq) needed to react completely with the sample of magnesium.

As the magnesium reacts, the hydrogen gas produced is collected by water displacement at 23.0 °C. The pressure of the gas in the collection tube is measured to be 749 torr.

c. Given that the equilibrium vapor pressure of water is 21 torr at 23.0 °C, calculate the pressure that the $H_2(g)$ produced in the reaction would have if it were dry.

d. Calculate the volume, in liters measured at the conditions in the laboratory, that the $H_2(g)$ produced in the reaction would have if it were dry.

e. The laboratory procedure specified that the concentration of the HCl solution be 2.0 M, but only 12.3 M HCl was available. Describe the steps for safely preparing 50.0 mL of 2.0 M HCl(aq) using 12.3 M HCl solution and materials selected from the list below. Show any necessary calculation(s).

10.0 mL graduated cylinder	Distilled water	250 mL beakers	Balance
50.00 mL volumetric flask	Dropper		

Half-Reaction	$E°$ (V)
$2\,CO_2(g) + 12\,H^+(aq) + 12\,e^- \rightarrow C_2H_5OH(aq) + 3\,H_2O(l)$	−0.085
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	1.229

3-2 A student uses a galvanic cell to determine the concentration of ethanol, C_2H_5OH, in an aqueous solution. The cell is based on the half-cell reactions represented in the table above.

a. Write a balanced equation for the overall reaction that occurs in the cell.
b. Calculate E^o for the overall reaction that occurs in the cell.
c. A 10.0 ml sample of C_2H_5OH(aq) is put into the electrochemical cell. The cell produces an average current of 0.10 amp for 20. Seconds, at which point the C_2H_5OH(aq) has been totally consumed.
 i. Calculate the charge, in coulombs, that passed through the cell.
 ii. Calculate the initial [C_2H_5OH] in the solution.

An alternative approach to determine the concentration of $C_2H_5OH(aq)$ in a solution is based on the reaction represented below.

$$\underset{}{3\,C_2H_5OH(aq)} + \underset{orange}{2\,Cr_2O_7^{2-}(aq)} + 16\,H^+(aq) \rightarrow \underset{blue\text{-}green}{4\,Cr^{3+}(aq)} + 3\,CH_3COOH(aq) + 11\,H_2O(l)$$

A solution has an initial $Cr_2O_7^{2-}(aq)$ concentration of 1.0×10^{-3} *M* and an initial $C_2H_5OH(aq)$ concentration of 0.500 *M*. The solution contains enough strong acid to keep the pH essentially constant throughout the reaction. The student places a sample of the solution in a cuvette that has a path length of 0.50 cm and places it in a spectrophotometer set to measure absorbance at 440 nm. ($Cr_2O_7^{2-}(aq)$ is the only species in the reaction mixture that absorbs light at this wavelength.) The absorbance of $Cr_2O_7^{2-}(aq)$ in the solution is monitored as the reaction proceeds; the table below shows the absorbance as a function of time for the first trial.

Time (min)	Absorbance at 440 nm
0.00	0.782
1.50	0.553
3.00	0.389
4.50	0.278
6.00	0.194

(d) Calculate the value of [$Cr_2O_7^{2-}$] at 1.50 min.

(e) The student runs a second trial but this time uses a cuvette that has a path length of 1.00 cm. Describe how the experimental setup should be adjusted to keep the initial absorbance at 0.782. Justify your answer with respect to the factors that influence the absorbance of a sample in a spectrophotometer.

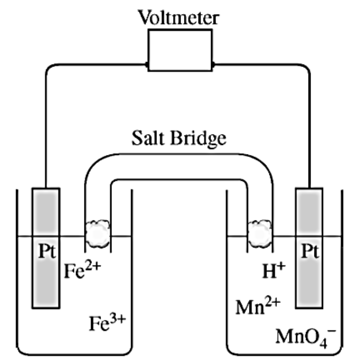
3-3 $XClO_3(s) \rightarrow XCl(s) + 3/2\,O_2(g)$

The equation above represents the decomposition of a compound containing an unknown element, X. A 1.39 g sample of XclO3(s) was completely decomposed by heating. The gas produced by the reaction was captured over water in a gas-collection tube at 24.0ºC. The total volume of gas in the tube was 506 mL, and the total pressure inside the tube was determine to be 739.5 torr. The vapor pressure of water is 22.4 torr at 24.0ºC.

a. Calculate the partial pressure, in torr, of the O_2 (g) that was collected at 24.0ºC.
b. Calculate the number of moles of O_2 (g) collected at 24.0ºC.
c. Determine the number of moles of $XClO_3$(s) that decomposed.
d. Determine the molar mass of the compound.
e. Determine the identity of element X.

3-4. 5 Fe^{2+}(aq) + MnO_4^- (aq) + 8 H^+(aq) → 5 Fe^{3+}(aq) + Mn^{2+}(aq) + $4H_2O$(l)

A galvanic cell and the balanced equation for the spontaneous cell reaction are shown. The two reduction half reactions for the overall reaction that occurs in the cell are shown in the table below.



Half reaction	***E*º (V) at 298 K**
Fe^{3+}(aq) + e^- → Fe^{2+}(aq)	**+ 0.77 V**
MnO_4^-(aq) + 8 H^+(aq) + 5 e^- → Mn^{2+}(aq) + 4 H_2O(l)	**+ 1.49 V**

a. Sketch drawing and clearly label the cathode.
b. Calculate the value of the standard potential, E^o, for the reaction.
c. How many moles of electrons are transferred when 1.0 mole of MnO_4^- (aq) is consumed in the overall cell reaction?
d. Calculate the value of the equilibrium constant, K_{eq}, for the cell reaction at 25 ºC. Explain what the magnitude of K_{eq} tells you about the extent of the reaction.
e. Indicate whether ΔG^o for this reaction is greater than 0, less than 0, or equal to 0. Justify your answer.

Three solutions, one containing Fe^{2+}(aq), one containing MnO_4^-(aq) and one containing H^+(aq), are mixed in a beaker and allowed to react. The initial concentrations of the species in the mixture are 0.60 M Fe^{2+}(aq), 0.10 M MnO_4^-(aq), and 1.0 M H^+(aq).

f. When the reaction mixture has come to equilibrium, which species has the higher concentration, Mn^{2+}(aq) or MnO_4^-(aq)? Explain.
g. When the reaction mixture has come to equilibrium, what are the molar concentrations of Fe^{2+}(aq) and Fe^{3+}(aq)?

3-5 A student is asked to prepare 100.0 mL of 1.000 x 10^{-2} M Na_2SO_4(aq) to use in a precipitation experiment. The student first weighs out 0.1429 g of solid Na_2SO_4.

a. The balance used to measure the mass of the Na_2SO_4 must have a certain minimum level of precision to ensure that the concentration of the solution can be known to four significant figures. If this minimum level is expressed as +/- x mg, what is the value of x?
b. Describe how the student can best prepare 100.0 mL of 1.000 x 10^{-2} M Na_2SO_4(aq) after the appropriate mass of solid Na_2SO_4 has been measured. From the list on the right, select the items to be used and describe the essential steps in the procedure for preparing the solution.

50 mL buret	100 mL Erlenmeyer flask	Distilled H_2O
50mL volumetric flask	100 mL volumetric flask	Dropper
100 mL beaker	100 mL graduate	
Squeeze bottle	10 mL volumetric pipet	

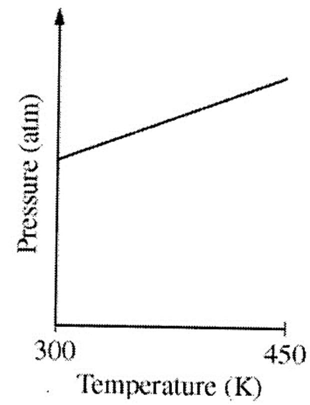
3-6. A sample of a pure, gaseous hydrocarbon is introduced into a previously evacuated rigid 1.00 L vessel. The pressure of the gas is 0.200 atm at a temperature of 127 ºC.

a) Calculate the number of moles of the hydrocarbon in the vessel.
b) O_2(g) is introduced into the same vessel containing the hydrocarbon. After the addition of the O_2(g), the total pressure of the gas mixture in the vessel is 1.40 atm at 127 ºC. Calculate the partial pressure of O_2(g) in the vessel.

The mixture of the hydrocarbon and oxygen is sparked so that a complete combustion reaction occurs, producing CO_2(g) and H_2O(g). The partial pressures of these gases at 127 ºC are 0.600 atm for CO_2(g) and 0.800 atm for H_2O(g). There is O_2(g) remaining in the container after the reaction is complete.

c) Use the partial pressures of CO_2(g) and H_2O(g) to calculate the partial pressure of the O_2(g) consumed in the combustion.
d) On the basis of your answers above, write the balanced chemical equation for the combustion reaction and determine the formula of the hydrocarbon.
e) Calculate the mass of the hydrocarbon that was combusted.
f) As the vessel cools to room temperature, droplets of liquid water form on the inside walls of the container. Predict whether the pH of the water in the vessel is less than 7, equal to 7, or greater than 7. Explain.

3-7 A sample of $C_2H_4(g)$ is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph on the right.



a. Describe TWO reasons why the pressure changes as the temperature of the $C_2H_4(g)$ increases. Your descriptions must be in terms of what occurs at the molecular level.

$C_2H_4(g)$ reacts readily with HCl(g) to produce $C_2H_5Cl(g)$, as represented by the following equation.

$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$ $\Delta H^o = - 72.6$ kJ / mol_{rxn}

b. When HCl(g) is injected into the container of $C_2H_4(g)$ at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level.

Multiple Choice Questions

3-8. Contains an element in a +1 oxidation state

a. CO_2 b. PbO_2 c. CaO d. N_2O_5 e. Cu_2O

Questions 3-9->3-10 refer to the chemical reactions represented below.

a. $C_2H_3O_2^-(aq) + H_3O^+(aq) \rightarrow HC_2H_3O_2(aq) + H_2O(l)$
b. $4\ H^+(aq) + 4\ Co^{2+}(aq) + O_2(g) + 24\ NH_3(aq) \rightarrow 4\ Co(NH_3)_6^{3+}(aq) + 2H_2O(l)$
c. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
d. $2\ H_2O_2(l) \rightarrow O_2(g) + 2\ H_2O(l)$

3-9. The reaction between a Brønsted-Lowry acid and a Brønsted-Lowry base
3-10. The reaction in which a single species is both oxidized and reduced

3-11. $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$

In the reaction represented above, what is the total number of moles of reactants consumed when 1.00 mole of $CO_2(g)$ is produced?

a. 0.33 mol b. 1.33 mol c. 1.50 mol d. 2.00 mol e. 6.00 mol

3-12 $H_2 + F_2 \rightarrow 2\ HF$

In the reaction represented above, what mass of HF is produced by the reaction of 3.0×10^{23} molecules of H_2 with excess F_2? (Assume the reaction goes to completion).

a. 1.0 g b. 4.0 g c. 10. g d. 20. g e. 40. G

3-13. … $LiHCO_3(aq)$ + … $H_2SO_4(aq) \rightarrow$ … $Li_2SO_4(aq) + H_2O(l)$ + … $CO_2(g)$

When the equation above is balanced and the coefficients are reduced to lowest whole number terms, what is the coefficient of $H_2O(l)$? a. 1 b. 2 c. 3 d. 4 e. 5

3-14. When a 3.22 g sample of an unknown hydrate of sodium sulfate, $Na_2SO_4 \cdot xH_2O(s)$, is heated, H_2O (molar mass 18 g) is driven off. The mass of the anhydrous $Na_2SO_4(s)$ (molar mass 142 g) that remains is 1.42 g. The value of x in the hydrate is a. 0.013 b. 1.8 c. 6.0 d. 10. e. 20.

3-15. What is the empirical formula of an oxide of chromium that is 48 percent oxygen by mass?

a. CrO b. CrO_2 c. CrO_3 d. Cr_2O e. Cr_2O_3

3-16. $2\ MnO_4^-(aq) + 5\ C_2O_4^{2-}(aq) + 16\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 8\ H_2O(l)$

Permanganate and oxalate ions react in an acidified solution according to the balanced equation above. How many moles of $CO_2(g)$ are produced when 20. mL of acidified 0.20 M $KMnO_4$ solution is added to 50. mL of 0.10 M $Na_2C_2O_4$ solution?

a. 0.0040 mol b. 0.0050 mol c. 0.0090 mol d. 0.010 mol e. 0.020 mol

3-17. Which of the following is NOT an accepted name for the formula given?

a. CH_3OH methanol b. CuO .. copper (I) oxide c. $FeCl_3$ .. iron (III) chloride

d. H_2SO_4 .. sulfuric acid e. $SrCO_3$ .. strontium carbonate

3-18. A student prepares a solution by dissolving 60.00 g of glucose (molar mass 180.2 g mol^{-1}) in enough distilled water to make 250.0 mL of solution. The molarity of the solution should be reported as

a. 12.01 M b. 12.0 M c. 1.332 M d. 1.33 M e. 1.3 M

3-19 A 0.35 g sample of Li(s) is placed in an Erlenmeyer flask containing 100 mL of water at 25oC. A balloon is placed over the mouth of the flask to collect the hydrogen gas that is generated. What will be the effect on the amount of gas produced if the experiment is repeated using 0.35 g of K(s) instead of 0.36 g of Li(s)?

a. No gas will be produced when K(s) is used.
b. Some gas will be produced but less than the amount of gas produced with Li(s).
c. Equal quantities of gas will be produced with the two metals.
d. More gas will be produced with K(s) than with Li(s).

3-20 Which of the following is the balanced net-ionic equation for the reaction between Li(s) and water?

(A) $2\,Li(s) + 2\,H^+(aq) + 2\,OH^-(aq) \rightarrow 2\,Li^+(aq) + 2\,OH^-(aq) + H_2(g)$

(B) $2\,Li(s) + 2\,H_2O(l) \rightarrow 2\,Li^+(aq) + 2\,OH^-(aq) + H_2(g)$

(C) $2\,Li(s) + 2\,H_2O(l) \rightarrow 2\,LiOH(s) + H_2(g)$

(D) $2\,Li(s) + 2\,H_2O(l) \rightarrow 2\,LiH(s) + H_2(g)$

3-21. When 200. mL of 2.0 M NaOH(aq) is added to 500. mL of 1.0 M HCl(aq), the pH of the resulting mixture is closest to a. 1.0 b. 3.0 c. 7.0 d. 13.0

$$X(g) + 2Y\,(g) \rightarrow XY_2(g)$$

3-22 In order to determine the order of the reaction represented above, the initial rate of formation of XY2 is measured using different initial values of [X] and [Y]. The results of the experiment are shown in the table below. **In trial 2 which of the reactants would be consumed more rapidly, and why?**

Trial	[X]	[Y]	Initial Rate of Formation of XY_2 ($M\,s^{-1}$)
1	0.50	0.50	8.0×10^{-3}
2	1.00	0.50	3.2×10^{-2}
3	1.00	1.00	6.4×10^{-2}

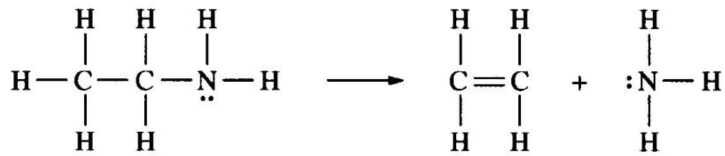
a. X, because it has a higher molar concentration.
b. X, because the reaction is second order with respect to X.
c. Y, because the reaction is second order with respect to Y.
d. Y, because the rate of disappearance will be double that of X.

Big Idea 4: Rates of chemical reactions are determined by details of the molecular collisions

Free Response Questions

4-1

An experiment is carried out to measure the rate of the reaction on the right, which is first order. A 4.70 x 10^{-3} mol sample of $CH_3CH_2NH_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $CH_3CH_2NH_2$ is found to be 3.60 x 10^{-4} mol/L.



d. Calculate the rate constant for the reaction at 773 K. Include units with your answer.

e. Calculate the initial rate, in M min^{-1}, of the reaction at 773 K.

f. If $\frac{1}{[CH_3CH_2NH_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

4-2 The gas phase decomposition of nitrous oxide has the following two step mechanism.

Step 1 $N_2O \rightarrow N_2 + O$

Step 2 $O + N_2O \rightarrow N_2 + O_2$

f. Write the balanced equation for the overall reaction.

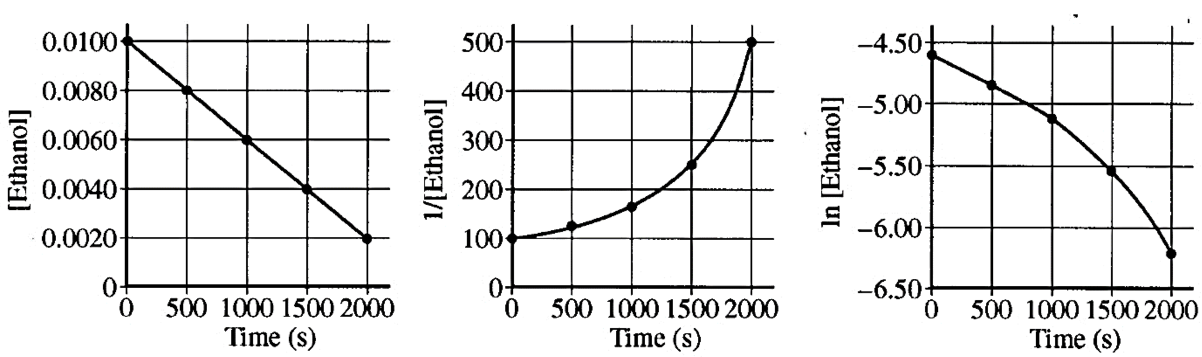
g. Is the oxygen atom, O, a catalyst for the reaction or is it an intermediate? Explain.

h. Identify the slower step in the mechanism if the rate law for the reaction was determined to be rate = k [N_2O]. Justify your answer

4-3 A sample of ethanol gas and a copper catalyst are placed in a rigid, empty 1.0 L flask. The temperature of the flask is held constant, and the initial concentration of the ethanol gas is 0.0100 M. The ethanol begins to decompose according to the chemical reaction represented below.

$$CH_3CH_2OH(g) \xrightarrow{Cu} CH_3CHO(g) + H_2(g)$$

The concentration of ethanol gas over time is used to create the three graphs below.



c. Given that the reaction order is zero, one, or two, use the information in the graphs to respond to the following.

   i. Determine the order of the reaction with respect to ethanol. Justify your answer.

   ii. Write the rate law for the reaction.

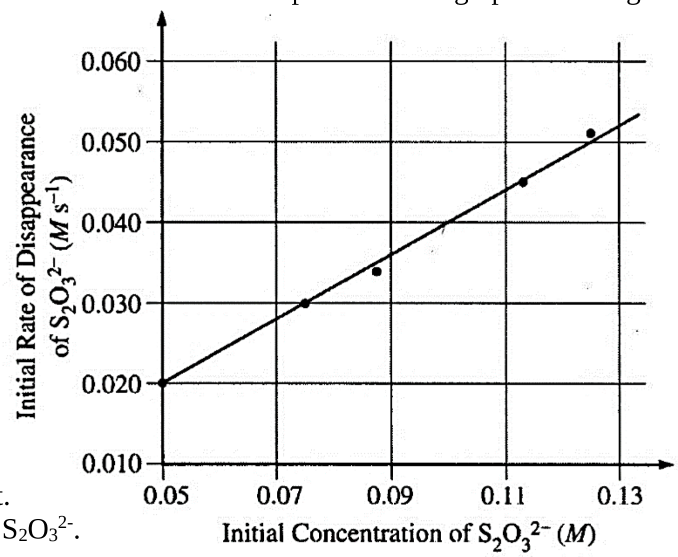
   iii. Determine the rate constant for the reaction, including units.

d. The pressure in the flask at the beginning of the experiment is 0.40 atm. If the ethanol completely decomposes, what is the final pressure in the flask?

4-4 $S_2O_3^{2-}(aq) \rightarrow SO_3^{2-}(aq) + S(s)$ in acidic solution

A student performed an experiment to investigate the decomposition of sodium thiosulfate, $Na_2S_2O_3$, in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of $S_2O_3^{2-}(aq)$. Data from five trials are given below in the table on the left and are plotted in the graph on the right.

Trial	Initial Concentration of $S_2O_3^{2-}$ (*aq*) (*M*)	Initial Rate of Disappearance of $S_2O_3^{2-}$ (*aq*) ($M\,s^{-1}$)
1	0.050	0.020
2	0.075	0.030
3	0.088	0.034
4	0.112	0.045
5	0.125	0.051



a. Identify the independent variable in the experiment.
b. Determine the order of the reaction with respect to $S_2O_3^{2-}$. Justify your answer by using the information above.
c. Determine the value of the rate constant, *k*, for the reaction. Include units in your answer. Show how you arrived at your answer.
d. In another trial the student mixed 0.10 M $Na_2S_2O_3$ with hydrochloric acid. Calculate the amount of time it would take for the concentration of $S_2O_3^{2-}$ to drop to 0.020 M.
e. On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials

$$2\,NO(g) + Br_2(g) \rightarrow 2\,NOBr(g)$$

4-5 3. $NO(g)$ reacts with $Br_2(g)$, as represented by the equation above. An experiment was performed to study the rate of the reaction at 546 K. Data from three trials are shown in the table below.

Trial	Initial [NO] (*M*)	Initial [Br_2] (*M*)	Initial Rate of Consumption of Br_2 ($M\,s^{-1}$)
1	0.10	0.20	12.0
2	0.40	0.20	192.0
3	0.10	0.60	36.0

a. Using the data in the table, determine the order of the reaction with respect to each of the following reactants. In each case, justify your answer, either with math or in words.
 i. Br_2 ii. NO
b. Write the rate law for the reaction.
c. Determine the value of the rate constant, k, for the reaction. Include units with your answer.
e. At a later time during trial 2, the concentration of $Br_2(g)$ is determined to be 0.16M.
 i. Determine the concentration of NO(g) at that time.
 ii. Calculate the rate of consumption of Br_2 at that time.

f. A proposed 2-step mechanism for the reaction is represented below.

Step 1: $NO + Br_2 \rightarrow NOBr_2$ slow (rate-determining step)
Step 2: $NO + NOBr_2 \rightarrow 2\,NOBr$ fast

Is the proposed mechanism consistent with the rate law determine in part b? Justify your answer.

Multiple Choice Questions

4-6 A 0.35 g sample of Li(s) is placed in an Erlenmeyer flask containing 100 mL of water at 25oC. A balloon is placed over the mouth of the flask to collect the hydrogen gas that is generated. Which of the following changes will most likely increase the rate of reaction between Li(s) and water?

a. Using 125 mL of water instead of 100 mL
b. Using a 0.25 g sample of Li(s) instead of a 0.35 g sample
c. Using a 0.35 g sample of Li(s) cut into small pieces
d. Decreasing the water temperature before adding the Li(s)

$$C_2H_4(g) + H_2 \xrightarrow{\text{platinium}} C_2H_6(g)$$

4-7 $C_2H_4(g)$ is reduced by $H_2(g)$ in the presence of a solid platinum catalyst, as represented by the equation above. Factors that could affect the rate of the reaction include which of the following?

I. Changes in the partial pressure of $H_2(g)$
II. Changes in the particle size of the platinum catalyst
III. Changes in the temperature of the reaction system

a. III only b. I and II only c. I and III only d. II and III only e. I, II, and III

4-8 The data in the table above were obtained for the reaction $X + Y \rightarrow Z$. Which of the following is the rate law for the reaction?

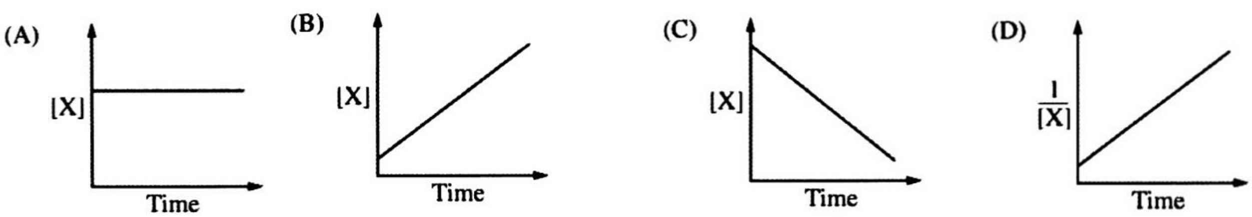
a. Rate = $k[X]^2$
b. Rate = $k[Y]^2$
c. Rate = $k[X][Y]$
d. Rate = $k[X]^2[Y]$

Exp.	Initial [*X*] (mol L^{-1})	Initial [Y] (mol L^{-1})	Initial Rate of Formation of Z (mol L^{-1} s^{-1})
1	0.10	0.30	4.0×10^{-4}
2	0.20	0.60	1.6×10^{-3}
3	0.20	0.30	4.0×10^{-4}

4-9. If the oxygen isotope ^{20}O has a half-life of 15 seconds, what fraction of a sample of pure ^{20}O remains after 1.0 minute? a. ½ b. ¼ c. 7/30 d. 1/8 e. 1/16

$$X \rightarrow \text{products}$$

4-10. Pure substance X decomposes according to the equation above. Which of the following graphs indicates that the rate of decomposition is second order in X?



4-11. The role of a catalyst in a chemical reaction is to

a. decrease the amount of reactants that must be used
b. lower the activation energy for the reaction
c. supply the activation energy required for the reaction to proceed
d. increase the amounts of products formed at equilibrium
e. increase the entropy change for the reaction

Question 4-12 to 4-14 refer to the following information

When free Cl(g) atoms encounter O_3(g) molecules in the upper atmosphere, the following reaction mechanism is proposed to occur.

$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$ *slow step*

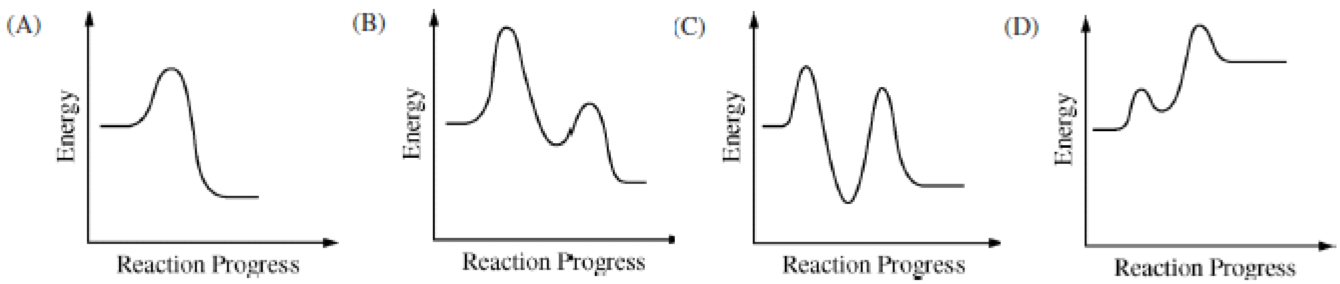
$\underline{ClO(g) + O_3(g) \rightarrow Cl(g) + 2O_2(g)}$ *fast step*

$2O_3(g) \rightarrow 3\ O_2(g)$ *overall reaction* ΔH = -285kJ/mol

4-12 Which of the following rate laws for the overall reaction corresponds to the proposed mechanism?
a) Rate = $k[O_3]^2$ b. Rate = $k[O_3]$ [Cl] c. Rate = $k[O_3]^2[ClO]$ d. Rate = $k[O_2]^3/[O_3]^2$

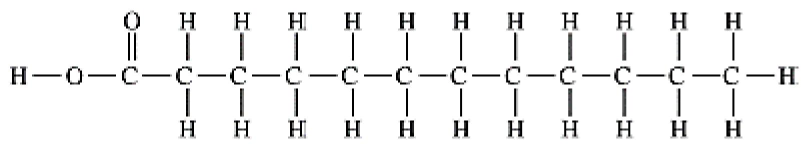
4-13 Which of the following is evidence that the mechanism is occurring?
a. The presence of Cl(g) increases the rate of the overall reaction.
b. The presence of Cl(g) decreases the rate of the overall reaction.
c. The presence of Cl(g) increases the equilibrium constant of the overall reaction.
d. The presence of Cl(g) decreases the equilibrium constant of the overall reaction.

4-14 Which of the following reaction energy profiles best corresponds to the propose mechanism?

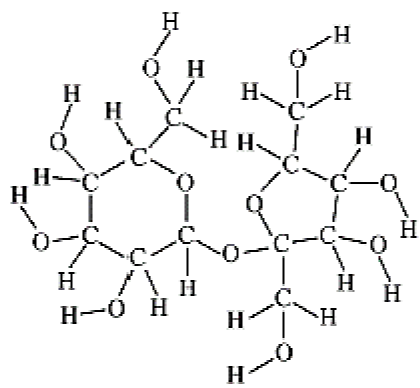


Big Idea 5: The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter

Free Response Questions



Lauric Acid



Sucrose

5-1 The structures of two compounds commonly found in food, lauric acid, $C_{12}H_{24}O_2$, and sucrose, $C_{12}H_{22}O_{11}$ are shown above.

a. Which compound is more soluble in water? Justify your answer in terms of the intermolecular forces present between water and each of the compounds.

b. Assume that a 1.5 g sample of lauric acid is combusted and all of the heat energy released is transferred to a 325 g sample of water initially at 25ºC. Calculate the final temperature of the water if $\Delta H_{combustion}$ of lauric acid is -37 kJ/g and the specific heat of water is 4.18 J/(g*K).

c. In an attempt to determine $\Delta H_{combustion}$ of lauric acid experimentally, a student places a 1.5 g sample of lauric acid in a ceramic dish underneath a can made of Al containing 325 g of water at 25Oc. The student ignites the sample of lauric acid with a match and records the highest temperature reached by the water in the can.

i) The experiment is repeated using a can of the same mass, but this time the can is made of Cu. The specific heat of Cu is 0.39 J/(g*K) and the specific heat of Al is 0.90 J/(g*K). Will the final temperature of the water in the can made of Cu be greater than, less than, or equal to the final temperature of the water in the can made of Al? Justify your answer.

ii) In both experiments it was observed that the measured final temperature of the water was less than the final temperature calculated in part (b). Identify one source of experimental error that might account for this discrepancy and explain why the error would bake the measured final temperature of the water lower than predicted.

d. The experiment described above is repeated using a 1.5 g sample of sucrose. The combustion reaction for sucrose in air is represented below.

$$C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(g)$$

i. Even though ΔG^o for the combustion of sucrose in air has a value of -5837kJ/Molrxn, the combustion reaction does not take place unless it is ignited. Explain.

ii. Predict the sign of ΔS^o for the reaction and justify your prediction.

5-2 $CaSO_4 \bullet 2H_2O(s) \rightarrow CaSO_4(s) + 2\ H_2O(g)$

The hydrate $CaSO_4 \bullet 2H_2O(s)$ can be heated to form the anhydrous salt, $CaSO_4(s)$, as shown by the reaction represented above.

Substance	ΔG_f^o at 298 K (kJ / mol)
$CaSO_4 \bullet 2H_2O(s)$	-1795.70
$CaSO_4(s)$	-1320.30
$H_2O(g)$	-228.59

a. Using the data in the table on the right, calculate the value of ΔG^o, in kJ / mol_{rxn}, for the reaction at 298 K.

b. Given that the value of ΔH^o for the reaction at 298 K is +105 kJ / mol_{rxn}, calculate the value of ΔS^o for the reaction at 298 K. Include units with your answer.

5-3 Answer the following questions about nitrogen, hydrogen, and ammonia.

a. Draw the complete Lewis electron-dot diagrams for N_2 and NH_3.

b. Calculate the standard free energy change, ΔG^o, that occurs when 12.0 g of $H_2(g)$ reacts with excess $N_2(g)$ at 298 K according to the reaction represented below.

$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g) \qquad \Delta G_{298}^o = -34\ kJ\ mol^{-1}$

c. Given that ΔH_{298}^o for the reaction is $-92.2\ kJ\ mol^{-1}$, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

d. The value of the standard entropy change, ΔS_{298}^o, for the reaction is $-199\ J\ mol^{-1}\ K^{-1}$. Explain why the value of ΔS_{298}^o is negative.

e. Assume that ΔH^o and ΔS^o for the reaction are independent of temperature.

i. Explain why there is a temperature above 298 K at which the algebraic sign of the value of ΔG^o changes.

ii. Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

5-4 $XClO_3(s) \rightarrow XCl(s) + 3/2\ O_2(g)$

In an experiment, 0.470 mol of XClO3(s) decomposed at 1.0 atm in the presence of a catalyst as a total of 21.1 kJ of heat was released. The value of ΔG^o for the reaction is -121.5 kJ/mol.

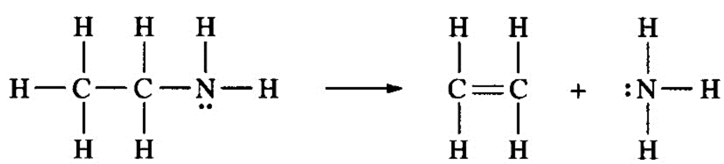
f. Calculate the value of ΔH^o for the decomposition reaction.

g. Which is larger: the sum of the bond energies of the products or the sum of the bond energies of the reactants. Justify your answer.

h. How does the presence of a catalyst affect the value of ΔG^o for this reaction. Justify your answer.

5-5 A sample of $CH_3CH_2NH_2$ is placed in an insulated container, where it decomposes into ethane and ammonia according to the reaction represented below.

Substance	Absolute Entropy, S^o in $J\ mol^{-1}\ K^{-1}$ at 298 K
$CH_3CH_2NH_2(g)$	284.9
$CH_2CH_2(g)$	219.3
$NH_3(g)$	192.8



a) Using the data in the table above, calculate the value, in J/ (mol K), of the standard entropy change, ΔS^o, for the reaction at 298 K.

b) Using the data in the table below, calculate the value, in kJ/mol_{rxn}, of the standard enthalpy change, ΔH^o, for the reaction at 298 K.

Bond	C – C	C = C	C – H	C – N	N – H
Average Bond Enthalpy(kJ/mol)	348	614	413	293	391

c) Based on your answer to part b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

Multiple Choice Questions

5-6. Which of the following processes involves the greatest increase in entropy?

a. $SO_3(g) + H_2(g) \rightarrow SO_2(g) + H_2O(g)$ b. $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ c. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

d. $C_2H_2(g) + 2\ H_2(g) \rightarrow C_2H_6(g)$ e. $MgSO_3(s) \rightarrow MgO(s) + SO_2(g)$

$$\mathbf{2\ NH_3(g) \rightarrow 3\ H_2(g) + N_2(g)\quad \Delta H^o_{298} = 92\ kJ/mol_{rxn}}$$

5-7. According to the information above, what is the standard enthalpy of formation, ΔH_f^o, for $NH_3(g)$ at 298 K ?

a. −92 kJ/mol b. −46 kJ/mol c. 46 kJ/mol d. 92 kJ/mol e. 184 kJ/mol

5-8. In an insulated cup of negligible heat capacity, 50. g of water at 40.°C is mixed with 30. g of water at 20.°C. The final temperature of the mixture is closest to

a. 22°C b. 27°C c. 30.°C d. 33°C e. 38°C

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$

5-9. For the reaction represented above at 25°C, what are the signs of $\Delta H°$, $\Delta S°$, and $\Delta G°$?

	ΔH^o	ΔS^o	ΔG^o		ΔH^o	ΔS^o	ΔG^o
a.	+	+	+	d.	-	-	-
b.	+	+	-	e.	-	-	+
c.	+	-	-				

5-10. Under which of the following conditions can an endothermic reaction be thermodynamically favorable?

a. ΔG is positive b. ΔS is negative c. $T\ \Delta S > \Delta H$ d. $T\Delta S = 0$

e. There are no conditions under which an endothermic reaction can be thermodynamically favorable.

5-11. $$4\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ N_2(g) + 6\ H_2O(g)$$

If the standard molar heats of formation of ammonia, $NH_3(g)$, and gaseous water, $H_2O(g)$, are -46 kJ /mol and -242 kJ /mol, respectively, what is the value of ΔH_{298}^o for the reaction represented above?

a. -190 kJ / mol_{rxn} b. -290 kJ / mol_{rxn} c. -580 kJ / mol_{rxn} d. -1270 kJ / mol_{rxn} e. -1640 kJ / mol_{rxn}

5-12. When a magnesium wire is dipped into a solution of lead (II) nitrate, a black deposit forms on the wire. Which of the following can be concluded from this observation?

a. The standard reduction potential, E^o, for $Pb^{2+}(aq)$ is greater than that for $Mg^{2+}(aq)$.
b. Mg(s) is less easily oxidized than Pb(s)
c. An external source of potential must have been supplied.
d. The magnesium wire will be the cathode of a Mg / Pb cell.
e. Pb(s) can spontaneously displace $Mg^{2+}(aq)$ from solution.

5-13 $$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(g)\quad \Delta H < 0$$

The synthesis of $CH_3OH(g)$ from CO(g) and $H_2(g)$ is represented by the equation above. The value of K_c for the reaction at 483 K is 14.5.

Which of the following statements is true about bond energies in this reaction?

a. The energy absorbed as the bonds in the reactants are broken is greater than the energy released as the bonds in the product are formed.
b. The energy released as the bonds in the reactants are broken is greater than the energy absorbed as the bonds in the product are formed.
c. The energy absorbed as the bonds in the reactants are broken is less than the energy released as the bonds in the product are formed.
d. The energy released as the bonds in the reactants are broken is less than the energy absorbed as the bonds in the product are formed.

5-14. A 0.5 mol sample of He(g) and a 0.5 mol sample of Ne(g) are placed separately in two 10.0 L rigid containers at 25oC. Each container has a pinhole opening. Which of the gases, He(g) or Ne(g), will escape faster through the pinhole and why?

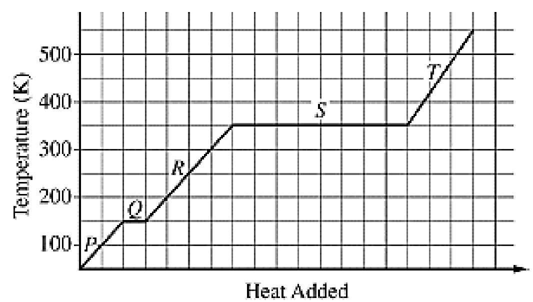
a. He will escape faster because the He atoms are moving at a higher average speed than the Ne atoms.
b. Ne will escape faster because its initial pressure in the container is higher.
c. Ne will escape faster because the Ne atoms have a higher average kinetic energy than the He atoms.
d. Both gases will escape at the same rate because the atoms of both gases have the same average kinetic energy.

5-15 $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ $\Delta H^o_{298} = -92$ kJ / mol_{rxn}; $\Delta G^o_{rxn} = -33$ kJ / mol_{rxn}

Consider the reaction represented above at 298 K. When equal volumes of $N_2(g)$ and $H_2(g)$, each at 1 atm, are mixed in a closed container at 298 K, no formation of $NH_3(g)$ is observed. Which of the following best explains the observation?

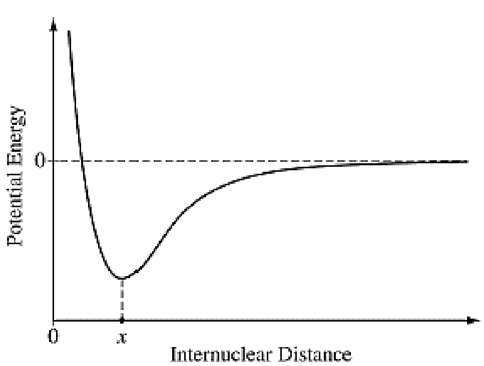
a. The $N_2(g)$ and the $H_2(g)$ must be mixed in a 1:3 ratio for a reaction to occur.
b. A high activation energy makes the forward reaction extremely slow at 298 K.
c. The reaction has an extremely small equilibrium constant, thus almost no product will form.
d. The reverse reaction has a lower activation energy than the forward reaction, so the forward reaction does not occur.

5-16 A hot iron ball is dropped into a 200. g sample of water initially at 50.°C. If 8.4 kJ of heat is transferred from the ball to the water, what is the final temperature of the water? (The specific heat of water is 4.2 J/(g*°C.) a. 40. °C b. 51°C c. 60. °C d. 70. °C



15-17 The heating curve for a sample of pure ethanol is provided above. The temperature was recorded as a 50.0g sample of solid ethanol was heated at a constant rate. Which of the following explains why the slope of segment T is greater than the slope of segment R?

a. The specific heat capacity of the gaseous ethanol is less than the specific heat capacity of liquid ethanol.
b. The specific heat capacity of gaseous ethanol is greater than the specific heat capacity of liquid ethanol.
c. The heat of vaporization of ethanol is less than the heat of fusion of ethanol.
d. The heat of vaporization of ethanol is greater than the heat of fusion of ethanol.



5-18 The potential energy of a system of two atoms as a function of their intermolecular distance is shown in the diagram above. Which of the following is true of the forces between the atoms when their internuclear distance is x?

a. The attractive and repulsive forces are balanced, so the atoms will maintain an average internuclear distance x.
b. There is a net repulsive force pushing the atoms apart, so the atoms will move further apart.
c. There is a net attractive force pulling the atoms together, so the atoms will move closer together.
d. In cannot be determined whether the forces between atoms are balanced, attractive, or repulsive, because the diagram shows only potential energy.

Big Idea 6: Any bond or intermolecular attraction that can be formed can be broken. These two processes are in a dynamic competition, sensitive to initial conditions and external perturbations.
Free Response Questions

$$HC_9H_7O_4(aq) + H_2O(l) \leftrightarrow H_3O^+ (aq) + C_9H_7O_4^-(aq)$$

6-1 The molecular formula of acetylsalicylic acid, also known as aspirin, is $HC_9H_7O_4$**.** The dissociation of $HC_9H_7O_4(aq)$ is represented by the equation above. The H of 0.0100 M $HC_9H_7O_4(aq)$ is measured to be 2.78.

a. Write the expression for the equilibrium constant, K_a, for the reaction above.
b. Calculate the K_a for acetylsalicylic acid.
c. An aqueous solution of aspirin is buffered to have equal concntraion of $HC_9H_7O_4(aq)$ and $C_9H_7O_4^{-1}(aq)$. Calculate the pH of the solution.

6-2. The compound butane, C_4H_{10}, occurs in two isomeric forms, *n*-butane and isobutane (2-methyl propane). Both compounds exist as gases at 25 °C and 1.0 atm.

a. Draw the structural formula of each of the isomers (include all atoms). Clearly label each structure.
b. On the basis of molecular structure, identify the isomer than has the higher boiling point. Justify your answer.

The two isomers exist in equilibrium as represented by the equation below.

***n*-butane(g) →isobutane(g)** $K_c = 2.5$ at 25 °C

Suppose that a 0.010 mol sample of pure *n*-butane is placed in an evacuated 1.0 L rigid container at 25 °C.

c. Write the expression for the equilibrium constant, K_c, for the reaction.
d. Calculate the initial pressure in the container when the *n*-butane is first introduced (before the reaction starts).
e. The *n*-butane reacts until equilibrium has been established at 25 °C.
   i. Calculate the total pressure in the container at equilibrium. Justify your answer.
   ii. Calculate the molar concentration of each species at equilibrium.
   iii. If the volume of the system is reduced to half of its original volume, what will the new concentration of *n*-butane after equilibrium has been reestablished at 25 °C? Justify your answer.

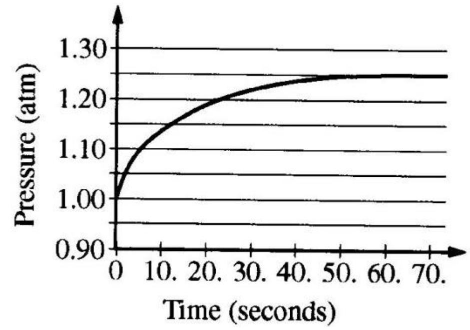
Suppose that in another experiment a 0.010 mol sample of pure isobutane is placed in an evacuated 1.0 L rigid container and allowed to come to equilibrium at 25 °C.

f. Calculate the molar concentration of each species after equilibrium has been established.

6-3 A pure 14.85 g sample of the weak base ethylamine, $C_2H_5NH_2$, is dissolved in enough water to make 500. mL of solution.

a. Calculate the molar concentration of the $C_2H_5NH_2$ in the solution.
   The aqueous ethylamine reacts with water according to the equation below.
   $$C_2H_5NH_2(aq) + H_2O(l) \leftrightarrow C_2H_5NH_3^+(aq) + OH^-(aq)$$
b. Write the equilibrium constant expression for the reaction between $C_2H_5NH_2(aq)$ and water.
c. Of $C_2H_5NH_2(aq)$ and $C_2H_5NH_3^+(aq)$, which is present in the solution at the higher concentration at equilibrium? Justify your answer.
d. A different solution is made by mixing 500. mL of 0.500 M $C_2H_5NH_2$ with 500. mL of 0.200 M HCl. Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.
   i. Calculate the concentration of $OH^-(aq)$ in the solution.
   ii. Write the net ionic equation that represents the reaction that occurs when the $C_2H_5NH_2$ solution is mixed with the HCl solution.
   iii. Calculate the molar concentration of the $C_2H_5NH_3^+(aq)$ that is formed in the reaction.
   iv. Calculate the value of K_b for $C_2H_5NH_2$.

6-4c. A small amount of liquid ethyl methanoate (boiling point 54 °C) was placed in a rigid closed 2.0 L container containing argon gas at an initial pressure of 1.00 atm and a temperature of 20 °C. The pressure in the container was monitored for 70. seconds after the ethyl methanoate was added, and the data in the graph below were obtained. It was observed that some liquid ethyl methanoate remained in the flask after 70.0 seconds. (Assume that the volume of the remaining liquid is negligible compared to the total volume of the container.)



i. Explain why the pressure in the flask increased during the first 60. seconds.

ii. Explain, in terms of processes occurring at the molecular level, why the pressure in the flask remained constant after 60. seconds.

iii. What is the value of the partial pressure of ethyl methanoate vapor in the container at 60. seconds?

iv. After 80. seconds, additional liquid ethyl methanoate is added to the container at 20 °C. Does the partial pressure of the ethyl methanoate vapor in the container increase, decrease, or stay the same? Explain. (Assume that the volume of the additional liquid ethyl methanoate in the container is negligible compared to the total volume of the container.)

6-5. Several reactions are carried out using AgBr, a cream-colored silver salt for which the value of the solubility-product constant, K_{sp}, is 5.0×10^{-13} at 298 K

a. Write the expression for the solubility-product constant, K_{sp}, of AgBr.

b. Calculate the value of $[Ag^+]$ in 50.0 mL of a saturated solution of AgBr at 298 K.

c. A 50.0 mL sample of distilled water is added to the solution described in part b, which is in a beaker with some solid AgBr at the bottom. The solution is stirred and equilibrium is reestablished. Some solid AgBr remains in the beaker. Is the value of $[Ag^+]$ greater than, less than, or equal to the value you calculated in part b? Justify your answer.

d. Calculate the minimum volume of distilled water, in liters, necessary to completely dissolve a 5.0 g sample of AgBr(s) at 298 K. (The molar mass of AgBr is 188 g mol^{-1}).

e. A student mixes 10.0 mL of 1.5×10^{-4} M $AgNO_3$ with 2.0 mL of 5.0×10^{-4} M NaBr and stirs the resulting mixture. What will the student observe? Justify you answer with calculations.

f. The color of another salt of silver, AgI(s) is yellow. A student adds a solution of NaI to a test tube containing a small amount of solid, cream-colored AgBr. After stirring the contents of the test tube, the student observes that the solid in the test tube changes color from cream to yellow.

i. Write the chemical equation for the reaction that occurred in the test tube.

ii. Which salt has the greater value of K_{sp}: AgBr or AgI? Justify your answer.

6-6 **The following questions apply to two isomers of $C_2H_4O_2$.**

O H

H C O C H

H

L

a. On your own paper, complete the Lewis electron-dot diagram of methyl methanoate in the box on the left. Show all valence electrons.

A student puts 0.020 mol of methyl methanoate into an evacuated rigid 1.0 L vessel at 40 K. The pressure is measured to be 0.74 atm. When the experiment is repeated using 0.020 mol of ethanoic acid using 0.020 mol of ethanoic acid instead of methyl methanoate, the measured pressure is lower than 0.74 atm. The lower pressure for ethanoic acid is due to the following reversible reaction.

$$CH_3COOH(g) + CH_3COOH(g) \rightleftarrows (CH_3COOH)_2(g)$$

b. Assume that when equilibrium has been reached, 50 percent of the ethanoic acid molecules have reacted.

i. Calculate the total pressure in the vessel at equilibrium at 450 K.

ii. Calculate the value of the equilibrium constant, K_p, for the reaction at 450 K.

6-7. Answer the following questions about the solubility and reactions of the ionic compounds $M(OH)_2$ and MCO_3, where M represents an unidentified metal.

a. Identify the charge of the M ion in the ionic compounds above.

b. At 25 °C, a saturated solution of $M(OH)_2$ has a pH of 9.15.

   i. Calculate the molar concentration of OH^-(aq) in the saturated solution.

   ii. Write the solubility product expression for $M(OH)_2$.

   iii. Calculate the value of the solubility product constant, K_{sp}, for $M(OH)_2$ at 25 °C.

c. For the metal carbonate, MCO_3, the value of the solubility product constant, K_{sp}, is 7.4 x 10^{-14} at 25 °C. On the basis of this information and your results in part b), which compound, $M(OH)_2$ or MCO_3, has the greater molar solubility in water at 25 °C? Justify your answer with a calculation.

d. MCO_3 decomposes at high temperatures, as shown by the reaction represented below.

$$\mathbf{MCO_3(s) \leftrightarrow MO(s) + CO_2(g)}$$

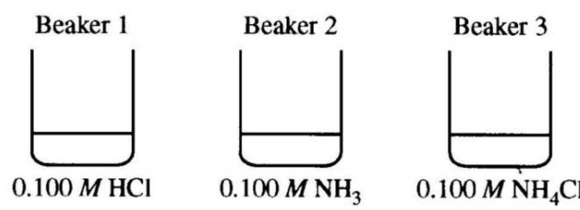
A sample of MCO_3 is placed in a previously evacuated container, heated to 423 K, and allowed to come to equilibrium. Some solid MCO_3 remains in the container. The value of K_P for the reaction at 423 K is 0.0012.

   i. Write the equilibrium constant expression for K_P of the reaction.

   ii. Determine the pressure, in atm, of CO_2(g) in the container at equilibrium at 423 K.

   iii. Indicate whether the value of ΔG^o for the reaction at 423 K is positive, negative, or zero. Justify your answer.

6-8 Each of three beakers contains 25.0 mL of a 0.100 M solution of HCl, NH_3, or NH_4Cl, as shown above. Each solution is at 25 °C.



a. Determine the pH of the solution in beaker 1. Justify your answer.

b. In beaker 2, the reaction $\mathbf{NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)}$ occurs. The value of K_b for NH_3(aq) is 1.8 x 10^{-5} at 25 °C.

   i. Write the K_b expression for the reaction of NH_3(aq) with H_2O(l).

   ii. Calculate the $[OH^-]$ in the solution in beaker 2.

c. In beaker 3, the reaction $NH_4^+(aq) + H_2O(l) \leftrightarrow NH_3(aq) + H_3O^+(aq)$ occurs.

   i. Calculate the value of K_a for NH_4^+ at 25 °C.

   ii. The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution.

d. The contents of beaker 1 are poured into the solution made in part c) ii). The resulting solution is stirred. Assume that volumes are additive.

   i. Is the resulting solution an effective buffer? Justify your answer.

   ii. Calculate the final $[NH_4^+]$ in the resulting solution at 25 °C.

6-9 $\mathbf{CH_3NH_2(aq) + H_2O(l) \leftrightarrow CH_3NH_3^+(aq) + OH^-(aq)}$ $K_b = 4.4 \times 10^{-4}$

The 50.0 mL sample of the methylamine solution is titrated with an HCl solution of unknown concentration. The equivalence point of the titration is reached after a volume of 36.0 mL of the HCl solution is added. The pH of the solution at the equivalence point is 5.98.

d. Write the net-ionic equation that represents the reaction that takes place during the titration.

e. Calculate the concentration of the HCl solution used to titrate the methylamine.

f. Sketch the titration curve that results from the titration described above. On the graph, clearly label the equivalence point of the titration.

6-10 A 1.22 g sample of a pure monoprotic acid, HA, was dissolved in distilled water. The HA solution was then titrated with 0.250 M NaOH. The pH was measured throughout the titration, and the equivalence point was reached when 40.0 mL of the NaOH solution had been added. The data from the titration are recorded in the table below.

Volume of 0.250 M NaOH Added (mL)	pH of titrated Solution
0.00	?
10.0	3.72
20.0	4.20
30.0	?
40.0	8.62
50.0	12.40

a. Explain how the data in the table above provide evidence that HA is a weak acid rather than a strong acid.
b. Write the balanced net-ionic equation for the reaction that occurs when the solution of NaOH is added to the solution of HA.
c. Calculate the number of moles of HA that were titrated.

d. Calculate the molar mass of HA. The equation for the dissociation reaction of HA in water is shown below.
   $HA(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + A^-(aq)$ $K_a = 6.3 \times 10^{-5}$
e. Assume that the initial concentration of the HA solution (before any NaOH solution was added) is 0.200 M. Determine the pH of the initial HA solution.
f. Calculate the value of $[H_3O^+]$ in the solution after 30.0 mL of NaOH is added and the total volume of the solution is 80.0 mL.

6-11 $NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$ Kp = .0792

When solid ammonium chloride is heated, it decomposes as represented above. The 10.0 g sample of solid ammonium chloride is placed in a rigid, evacuated 3.0 L container that is sealed and heated to 575K. The system comes to equilibrium with some solid ammonium chloride remaining in the container.

a. Write the expression for the equilibrium constant for the reaction in terms of partial pressure.
b. Calculate the partial pressure of ammonia, in atm, at equilibrium at 575K.
c. A small amount of ammonia is injected into the equilibrium mixture in the 3.0L container at 575K.
   i. As the new equilibrium is being established at 575K, does the amount of $NH_4Cl(s)$ in the container increase, decrease, or remain the same? Justify your answer.
   ii. After the new equilibrium is established at 575K, is the value of K_p greater than, less than, or equal to the value before the $NH_3(g)$ was injected into the container? Justify your answer.
d. When the temperature of the container is lowered to 500 K, the number of moles of $NH_3(g)$ in the container decreases. On the basis of this observation, is the decomposition of $NH_4Cl(s)$ endothermic or exothermic? Justify your answer.

In another experiment, 20.00 mL of .800M $NH_4Cl(aq)$ is prepared. The ammonium ion reacts with water according to the equation, $NH_4^+(aq) + H_20(l) \leftrightarrow NH_3(aq) + H_3O^+(aq)$.

e. Calculate the value of the equilibrium constant for the reaction of the ammonium ion with water. (At 25°C the value of the K_b is 1.8×10^{-5}).

6-12 (a) $Fe_2O_3(s)$ and $Al_2O_3(s)$ have similar chemical properties; some similarities are due to the oxides having similar lattice energies. Give two reasons why the lattice energies of the oxides are similar.

Use the following reactions that involve Fe and Al compounds to answer parts (b) and (c).

<u>In distilled water</u>

Reaction 1: $Fe_2O_3(s) + 3\ H_2O(l) \rightarrow 2\ Fe(OH)_3(s)$

Reaction 2: $Al_2O_3(s) + 3\ H_2O(l) \rightarrow 2\ Al(OH)_3(s)$

<u>In base</u>

Reaction 3: $Fe(OH)_3(s) + NaOH(aq) \rightarrow$ no reaction

Reaction 4: $Al(OH)_3(s) + NaOH(aq) \rightarrow NaAl(OH)_4(aq)$

<u>In acid</u>

Reaction 5: $Fe(OH)_3(s) + 3\ HCl(aq) \rightarrow FeCl_3(aq) + 3\ H_2O(l)$

Reaction 6: $Al(OH)_3(s) + 3\ HCl(aq) \rightarrow AlCl_3(aq) + 3\ H_2O(l)$

Reaction 7: $NaAl(OH)_4(aq) + HCl(aq) \rightarrow Al(OH)_3(s) + NaCl(aq) + H_2O(l)$

<u>When heated</u>

Reaction 8: $2\ Fe(OH)_3(s) \xrightarrow{heat} Fe_2O_3(s) + 3\ H_2O(g)$

Reaction 9: $2\ Al(OH)_3(s) \xrightarrow{heat} Al_2O_3(s) + 3\ H_2O(g)$

Compound	K_{sp}
$Fe(OH)_3$	4×10^{-38}
$Al(OH)_3$	1×10^{-33}

b.

The Ksp values for $Fe(OH)_3$ and $Al(OH)_3$ are given in the table above. A 1.0 g sample of powdered $Fe_2O_3(s)$ and a 1.0 g sample of powdered $Al_2O_3(s)$ are mixed together and placed in 1.0 L of distilled water.

i. Which ion, $Fe^{3+}(aq)$ or $Al^{3+}(aq)$, will be present in the higher concentration? Justify your answer with respect to the Ksp values provided.

ii. Write a balanced chemical equation for the dissolution reaction that results in the production of the ion that you identified in part (i).

c. Students are asked to develop a plan for separating $Al_2O_3(s)$ from a mixture of powdered Fe_2O_3 (s) and powdered Al_2O_3 using chemical reactions and laboratory techniques.

i. One student proposes that $Al_2O_3(s)$ can be separated by adding water to the mixture and then filtering. Explain why this approach is not reasonable.

ii. A second student organizes a plan using a table. The first two steps have already been entered in the table. As shown below. Complete the plan by listing additional steps that are needed to recover the Al_2O_3. List the remaining steps in the correct order and refer to the appropriate reaction from the original list by number, if applicable.

Step	Description	Reaction(s)
1	Add NaOH(aq) to convert Al_2O_3 (s) to $Al(OH)_3$ and then to $NaAl(OH)_4(aq)$	1 and 4
2	Filter out the solid $Fe(OH)_3$ from the mixture and save the filtrate.	-

iii. The second student recovers 5.5 g of $Al_2O_3(s)$ from a 10.0 g sample of the mixture. Calculate the percent of Al by mass in the mixture of the two powdered oxides. (The molar mass of Al_2O_3 is 101.96 g/mol, and the molar mass of $Fe_2O_3(s)$ is 159.70 g/mol.)

Multiple Choice Questions

6-13 An acetate buffer solution is prepared by combining 50. mL of 0.20 M acetic acid, $HC_2H_3O_2(aq)$, and 50. mL of 0.20 M sodium acetate, $NaC_2H_3O_2(aq)$. A 5.0 mL sample of 0.10 M NaOH(aq) is added to the buffer solution. Which of the following is a correct pairing of the acetate species present in greater concentration and of the pH of the solution after the NaOH(aq) is added? (The pKa of acetic acid is 4.7).

	Acetate Species	pH
A	$HC_2H_3O_2$	<4.7
B	$HC_2H_3O_2$	>4.7
C	$NaC_2H_3O_2$	<4.7
D	$NaC_2H_3O_2$	>4.7

6-14 $$\mathbf{Mg(OH)_2(s) \leftrightarrow Mg^{2+}(aq) + 2\ OH^{-1}(aq)}$$

The exothermic dissolution of $Mg(OH)_2(s)$ in water is represented by the equation above. The Ksp of $Mg(OH)_2$ is 1.8×10^{-11}. Which of the following changes will increase the solubility of $Mg(OH)_2$ in an aqueous solution?

a. Decreasing the pH c. adding NH_3 to the solution
b. Increasing the pH d. Adding $Mg(NO_3)_2$ to the solution

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \qquad K_{a_1} = 7.2 \times 10^{-3}$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-} \qquad K_{a_2} = 6.3 \times 10^{-8}$$
$$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-} \qquad K_{a_3} = 4.5 \times 10^{-13}$$

6-15 A solution is prepared by mixing 50 mL of 1 M NaH_2PO_4 with 50 mL of 1 M Na_2HPO_4. On the basis of the information above, which of the following species is present in the solution at the <u>lowest</u> concentration? a. Na^{1+} b. HPO_4^{2-} c. $H_2PO_4^{1-}$ d. PO_4^{3-}

$$\mathbf{2\ XY(g) \leftrightarrow X_2(g) + Y_2(g) \quad K_p = 230}$$

6-16 A certain gas, XY(g), decomposes as represented by the equation above. A sample of each of the three gases is put in a previously evacuated container. The initial partial pressures of the gases are shown in the table below.

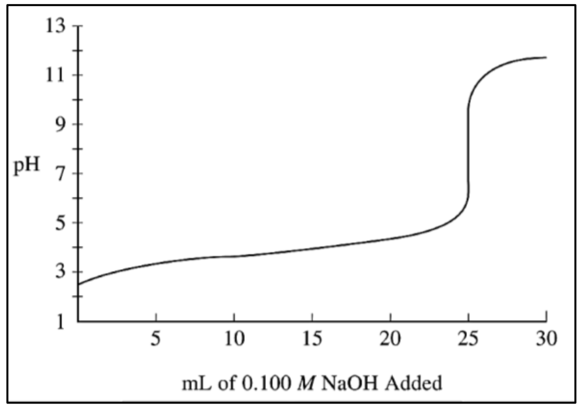
Gas	Initial Partial Pressure (atm)
XY	0.010
X_2	0.20
Y_2	2.0

The temperature of the reaction mixture is held constant. In which direction will the reaction proceed?

a. The reaction will form more products.
b. The reaction will form more reactant.
c. The mixture is at equilibrium, so there will be no change.
d. It cannot be determined unless the volume of the container is known.

6-17. An unknown acid is dissolved in 25 mL of water and titrated with 0.100 *M* NaOH. The results are shown in the titration curve above. Which of the following could be the unknown acid?

a. Fluoroacetic acid, $pK_a = 2.6$
b. Glycolic acid, $pK_a = 3.8$
c. Propanoic acid, $pK_a = 4.9$
d. Hypochlorous acid, $pK_a = 7.5$
e. Boric acid, $pK_a = 9.3$



6-18 Which of the following accounts for the observation that the pH of pure water at 37°C is 6.8?

a. At 37°C water is naturally acidic.
b. At 37°C the autoionization constant for water, Kw, is larger than it is at 25°C.
c. At 37°C water has a lower density than it does at 25°C; therefore, $[H^+]$ is greater.
d. At 37°C water ionizes to a lesser extent than it does at 25°C.

$$\mathbf{HF(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + F^{1-}(aq)}$$

6-19 The dissociation of the weak acid HF in water is represented by the equation above. Adding a 1.0 mL sample of which of the following would increase the percent ionization of HF(aq) in 10 mL of a solution of 1.0 M HF?

a. 1.0 M KF b. 1.0 M H_2SO_4 c. 10.0 M HF d. distilled water

Concentration (M)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
0.010	3.44	2.00	2.92	2.20
0.050	3.09	1.30	2.58	1.73
0.10	2.94	1.00	2.42	1.55
0.50	2.69	0.30	2.08	1.16
1.00	2.44	0.00	1.92	0.98

Use the table above to answer questions **6-20 to 6-22**

6-20 Of the following species, which has the greatest concentration in a 1.0 M solution of acid 1 at equilibrium? a. OH^- b. H_3O^+ c. Acid 1 d. The conjugate base of acid 1

6-21. If equal volumes of the four acids at a concentration of 0.50 M are each titrated with a strong base, which will require the greatest volume of base to reach the equivalence point?
a. Acid 1 b. Acid 2 c. Acid 3 d. All the acids

6-22. A 25 mL sample of a 1.0 M solution of acid 1 is mixed with 25 mL of 0.50 M NaOH. Which of the following best explains what happens to the pH of the mixture when a few drops of 1.0 M HNO_3 are added?

a. The pH of the mixture increases sharply, because HNO_3 is a strong acid.
b. The pH of the mixture decreases sharply, because H_3O^+ ions were added.
c. The pH of the mixture stays about the same, because the conjugate base of acid 1 reacts with the added H_3O^+ ions.
d. The pH of the mixture stays about the same, because the OH^- ions in the solution react with the added H_3O^+ ions.

$$X(g) + Y(g) \leftrightarrow 2\ Z(g)$$

6-23. When 4.00 mol each of X(*g*) and Y(*g*) are placed in a 1.00 L vessel and allowed to react at constant temperature according to the equation above, 6.00 mol of Z(*g*) is produced. What is the value of the equilibrium constant, K_c ?

a. 3 b. 6 c. 8 d. 16 e. 36

6-24. Caffeine ($C_8H_{10}N_4O_2$) is a weak base with a K_b value of 4 x 10^{-4}. The pH of a 0.01 M solution of caffeine is in the range of a. 2-3 b. 5-6 c. 7-8 d. 11-12

$$HX(aq) + Y^{-1}(aq) \leftrightarrow HY(aq) + X^{1-}(aq) \quad Keq>1$$

6-25. A solution of a salt of a weak acid HY is added to a solution of another weak acid HX. Based on the information given above, which of the following species is the strongest base?

a. HX(aq) b. Y^-(aq) c. HY(aq) d. X-(aq)

6-26. A solution containing HCl and the weak acid $HClO_2$ has a pH of 2.4. Enough KOH(aq) is added to the solution to increase the pH to 10.5. The amount of which of the following species increases as the KOH(aq) is added? a. Cl^-(aq) b. H^+(aq) c. ClO_2^-(aq) d. $HClO_2$(aq)

6-27.

$FeF_2(s) \leftrightarrow Fe^{2+}(aq) + 2F^-(aq)$ $K_1 = 2 \times 10^{-6}$

$F^-(aq) + H^+(aq) \leftrightarrow HF(aq)$ $K_2 = 1 \times 10^{3}$

$FeF_2(s) + 2\ H^+(aq) \leftrightarrow Fe^{2+}(aq) + 2\ HF(aq)$ $K_3 = ?$

On the basis of the information above, the dissolution of FeF_2(s) in acidic solution is

a. thermodynamically favorable, because $K_2 > 1$

b. thermodynamically favorable, because $K_3 > 1$

c. not thermodynamically favorable, because $K_1 < 1$

d. not thermodynamically favorable, because $K_3 < 1$

6-28. $2\ H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

The autoionization of water is represented by the equation above. Values of pK_w at various temperatures are listed in the table below.

Temperature (°C)	pK_w
0	14.9
10	14.5
20	14.2
30	13.8
40	13.5

Based on the information above, which of the following statements is true?

a. The dissociation of water is an exothermic process.

b. The pH of pure water is 7.00 at any temperature.

c. As the temperature increases, the pH of pure water increases.

d. As the temperature increases, the pH of pure water decreases.

Questions 6-29 to 6-30 refer to the following information.

$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(g) \quad \Delta H < 0$

The synthesis of $CH_3OH(g)$ from CO(g) and $H_2(g)$ is represented by the equation above. The value of K_c for the reaction at 483 K is 14.5.

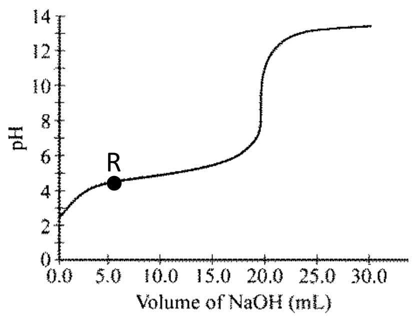
6-29 A 1.0 mol sample of CO(g) and a 1.0 mol sample of $H_2(g)$ are pumped into a rigid, previously evacuated 2.0 L reaction vessel at 483 K. Which of the following is true at equilibrium?

a. $[H_2] = 2\ [CO]$
b. $[H_2] < [CO]$
c. $[CO] = [CH_3OH] < [H_2]$
d. $[CO] = [CH_3OH] = [H_2]$

6-30 A mixture of CO(g) and $H_2(g)$ is pumped into a previously evacuated 2.0 L reaction vessel. The total pressure of the reaction system is 1.2 atm at equilibrium. What will be the total pressure of the system if the volume of the reaction vessel is reduced to 1.0 L at constant temperature?

a. Less than 1.2 atm
b. greater than 1.2 atm but less than 2.4 atm
c. 2.4 atm
d. greater than 2.4 atm

6-31



Use this titration curve for question 31 and 32. Data collected during the titration of a 20.0 mL sample of a 0.10 M solution of a monoprotic acid (HA) with a solution of NaOH of unknown concentration are plotted in the graph above. Based on the data, which of the following are the approximate pK_a of the acid and the molar concentration of the NaOH?

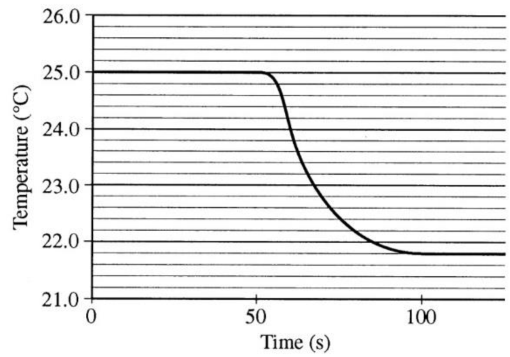
	pK_a	[NaOH]
a.	4.7	0.050 M
b.	4.7	0.10 M
c.	9.3	0.050 M
d.	9.3	0.10 M

6-32 At point R in the titration, which of the following species has the highest concentration?

a. HA b. A^{-1} c. $H3O^{+}$ d. OH^{-1}

Laboratory

Concepts – LABORATORY QUESTIONS – contained in several Big Ideas and the Science Practices



Free Response Questions

7-1 A student performs an experiment to determine the molar enthalpy of solution of urea, H_2NCONH_2. The student places 91.95 g of water at 25 °C into a coffee-cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25 °C, to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.

a. Determine the change in temperature of the solution that results from the dissolution of the urea.

b. According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

c. Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is 4.2 J g^{-1} $°C^{-1}$ throughout the experiment.
   i. Calculate the heat of dissolution of the urea in joules.
   ii. Calculate the molar enthalpy of solution, ΔH_{soln}^{o}, of urea in kJ mol^{-1}.

d. Using the information in the table below, calculate the value of the molar entropy of solution, ΔS_{soln}^{o}, of urea at 298 K. Include units with your answer.

	Accepted value
ΔH_{soln}^{o} of urea	14.0 kJ mol^{-1}
ΔG_{soln}^{o} of urea	-6.9 kJ mol^{-1}

e. The student repeats the experiment and this time obtains a result for ΔH_{soln}^{o} of urea that is 11 percent below the accepted value. Calculate the value of ΔH_{soln}^{o} that the student obtained in this second trial.

f. The student performs a third trial of the experiment but this time adds urea that has been taken directly from a refrigerator at 5 °C. What effect, in any, would using the cold urea instead of urea at 25 °C have on the experimentally obtained value of ΔH_{soln}^{o}? Justify your answer.

7-2. A student is instructed to prepare 100.0 mL of 1.250 M NaOH from a stock solution of 5.000 M NaOH. The student follows the proper safety guidelines.

a. Calculate the volume of 5.000 M NaOH needed to accurately prepare 100.0 mL of 1.250 M NaOH.

b. Describe the steps in a procedure to prepare 100.0 mL of 1.250 M NaOH using 5.000 M NaOH and equipment selected from the list below.

Balance	25 mL Erlenmeyer flask	100 mL graduated cylinder	100 mL volumetric flask
50 mL buret	100 mL Florence flask	25 mL pipet	100 mL beaker
Eyedropper	Drying oven	Wash bottle of distilled H_2O	Crucible

c. The student is given 50.0 mL of a 1.00 M solution of a weak, monoprotic acid, HA. The solution is titrated with the 1.250 M NaOH to the endpoint. (Assume that the endpoint is at the equivalence point.)

i. Explain why the solution is basic at the equivalence point of the titration. Include a chemical equation as part of your explanation.

ii. Identify the indicator in the table below that would be best for the titration. Justify your choice.

Indicator	pKa	Indicator	pKa
Methyl Red	5	Phenolphthalein	9
Bromothymol blue	7		

d. The student is given another 50.0 mL sample of 1.00 M HA, which the student adds to the solution that had been titrated to the endpoint in part c). The result is a solution with a pH of 5.0.

i. What is the value of the acid dissociation constant, K_a, for the weak acid? Explain your reasoning.

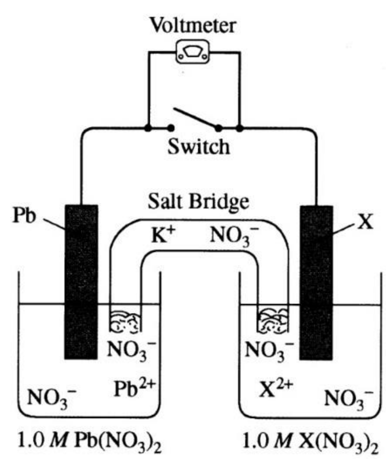
ii. Explain why the addition of a few drops of 1.250 M NaOH to the resulting solution does not appreciably change its pH.

7-3. In a laboratory experiment, Pb and an unknown metal Q were immersed in solutions containing aqueous ions of unknown metals Q and X. The following reactions summarize the observations.

Observation 1:	$Pb(s) + X^{2+}(aq) \rightarrow Pb^{2+}(aq) + X(s)$
Observation 2:	$Q(s) + X^{2+}(aq) \rightarrow$ no reaction
Observation 3:	$Pb(s) + Q^{2+}(aq) \rightarrow Pb^{2+}(aq) + Q(s)$

a. On the basis of the reactions indicated above, arrange the three metals, Pb, Q, and X, in order from least reactive to the most reactive.

The diagram below shows an electrochemical cell that is constructed with a Pb electrode immersed in 100. mL of 1.0 M $Pb(NO_3)_2(aq)$ and an electrode made of metal X immersed in 100. mL of 1.0 M $X(NO_3)_2(aq)$. A salt bridge containing saturated aqueous KNO_3 connects the anode compartment to the cathode compartment. The electrodes are connected to an external circuit containing a switch, which is open. When a voltmeter is connected to the circuit as shown, the reading on the voltmeter is 0.47 V. When the switch is closed, electrons flow through the switch from the Pb electrode toward the X electrode.



b. Write the equation for the half reaction that occurs at the anode.

c. The value of the standard potential for the cell, E^o, is 0.47 V.

i. Determine the standard reduction potential for the half reaction that occurs at the cathode.

ii. Determine the identity of metal X.

d. Describe what happens to the mass of each electrode as the cell operates.

7-4. A student is assigned the task of determining the mass percent of silver in an alloy of copper and silver by dissolving a sample of the alloy in excess nitric acid and then precipitating the silver as AgCl. First the student prepares 50. mL of 6 M HNO_3.

a. The student is provided with a stock solution of 16 M HNO_3, two 100 mL graduated cylinders that can be read to ± 1 mL, a 100 mL beaker that can be read to ± 10 mL, safety goggles, rubber gloves, a glass stirring rod, a dropper, and distilled H_2O.

i. Calculate the volume, in mL, of 16 M HNO_3 that the student should use for preparing 50. mL of 6 M HNO_3.
ii. Briefly list the steps of an appropriate and safe procedure for preparing the 50. mL of 6 M HNO_3. Only materials selected from those provided to the student (listed above) may be used.
iii. Explain why it is not necessary to use a volumetric flask (calibrated to 50.00 mL ± 0.05 mL) to perform the dilution.
iv. During the preparation of the solution, the student accidently spills about 1 mL of 16 M HNO_3 on the bench top. The student finds three bottles containing liquids sitting near the spill: a bottle of distilled water, a bottle of 5 percent $NaHCO_3$(aq), and a bottle of saturated NaCl(aq). Which of the liquids is best to use in cleaning up the spill? Justify your choice.

Then the student pours 25 mL of the 6 M HNO_3 into a beaker and adds a 0.6489 g sample of the alloy. After the sample completely reacts with the acid, some saturated NaCl(aq) is added to the beaker, resulting in the formation of an AgCl precipitate. Additional NaCl(aq) is added until no more precipitate is observed to form. The precipitate is filtered, dried, and weighed to constant mass in a filter crucible. The data are shown in the table below.

Mass of sample of copper - silver alloy	0.6489 g
Mass of dry filter crucible	28.7210 g
Mass of filter crucible and precipitate (1st weighing)	29.3587 g
Mass of filter crucible and precipitate (2nd weighing)	29.2599 g
Mass of filter crucible and precipitate (3rd weighing)	29.2598 g

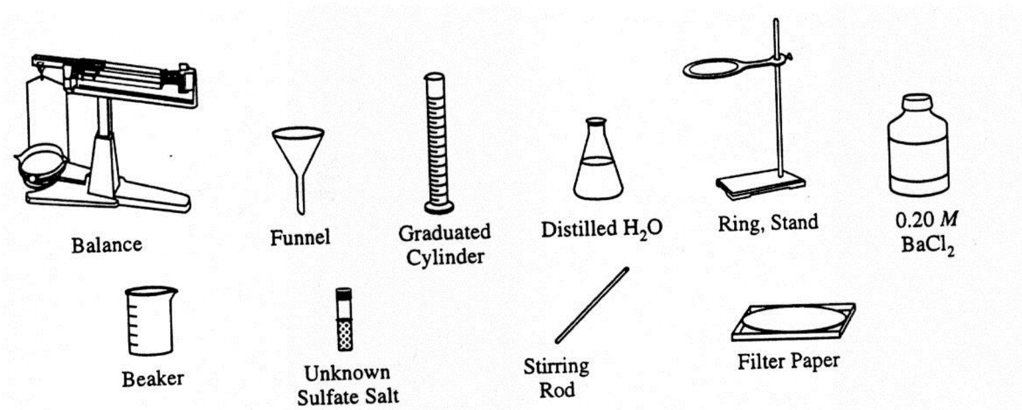
b. Calculate the number of moles of AgCl precipitate collected.
c. Calculate the mass percent of silver in the alloy of copper and silver.

7-5. Four bottles, each containing about 5 grams of finely powdered white substance, are found in a laboratory. Near the bottles are four labels specifying high purity and indicating that the substances are:

glucose ($C_6H_{12}O_6$), sodium chloride (NaCl), aluminum oxide (Al_2O_3), and zinc sulfate ($ZnSO_4$).

Assume that these labels belong to the bottles and that each bottle contains a single substance. Describe the tests you would conduct to determine which label belongs to which bottle. Give the results you would expect for each test.

7-6



An experiment is to be performed to determine the mass percent of sulfate in an unknown soluble sulfate salt. The equipment shown above is available for the experiment. A drying oven is also available.

(a) Briefly list the steps needed to carry out this experiment.
(b) What experimental data need to be collected to calculate the mass percent of sulfate in the unknown?
(c) List the calculations necessary to determine the mass percent of sulfate in the unknown.
(d) Would 0.20-molar $MgCl_2$ be an acceptable substitute for the $BaCl_2$ solution provided for this experiment? Explain.

Multiple Choice

7-7. For an experiment, a student needs 100.0 mL of 0.4220 *M* NaCl. If the student starts with NaCl(*s*) and distilled water, which of the following pieces of laboratory glassware should the student use to prepare the solution with the greatest accuracy?
a. 25 mL volumetric pipet
b. 100 mL Erlenmeyer flask
c. 100 mL graduated cylinder
d. 100 mL volumetric flask
e. 1 L beaker

7-8. The percentage of silver in a solid sample is determined gravimetrically by converting the silver to $Ag^+(aq)$ and precipitating it as silver chloride. Failure to do which of the following could cause errors?
I. Account for the mass of the weighing paper when determining the mass of the sample
II. Measure the temperature during the precipitation reaction
III. Wash the precipitate
IV. Heat the AgCl precipitate to constant mass

a. I only
b. I and II
c. I and IV
d. II and III
e. I, III, and IV

7-9. Potassium hydrogen phthalate, KHP, is used as a primary standard for determining the concentration of a solution of NaOH by titration. If the KHP has not been dried before weighing, the calculated molarity of the NaOH would be
a. higher than the actual value, since water is included in the apparent mass of KHP
b. higher than the actual value, since the presence of water requires a larger volume of titrant
c. lower than the actual value, since NaOH absorbs water
d. unaffected, since KHP is a strong acid
e. unaffected, since water is routinely added before the titration

7-10. $NaOH(aq) + HCl(aq) \rightarrow H_2O(l) + NaCl(aq)$

A student is trying to determine the heat of reaction for the acid-base neutralization reaction represented above. The student uses 0.50 *M* NaOH and 0.50 *M* HCl solutions. Which of the following situations, by itself, would most likely result in the LEAST error in the calculated value of the heat of reaction?
a. The thermometer was incorrectly calibrated and read 0.5 Celsius degree too high during the procedure.
b. The volume of the acid solution added to the calorimeter was actually 1.0 mL less than what was recorded.
c. The calorimeter was poorly insulated, and some heat escaped to the atmosphere during the procedure.
d. The actual molarity of the base solution was 0.53 *M* but was recorded as 0.50 *M*.

Test question source and MC answer key

Test Quest	Original Test	Test Ques	Original Test	Test Que	Original Test	Test Quest.	Original Test	Test Quest.	Original Test
1-1	1987-5	2-14	13I-71a	3-18	13I-74c	5-8	13I-46d	6-17	13I-56b
1-2	2015PR-6	2-15	13I-73b	3-19	15PR-18b	5-9	13I-52d	6-18	15PR-30b
1-3	2013I-6	2-16	13I-54d	3-20	15PR-20b	5-10	12I-31c	6-19	15PR-33d
1-4	13I-18e	2-17	15PR-4d	3-21	14-11a	5-11	12I-53d	6-20	13PR-50c
1-5	15PR-3d	2-18	15PR-5c	3-22	15PR-49d	5-12	12I-54a	6-21	13PR-51d
1-6	13PR-43d	2-19	14-17a	4-1	2012-3	5-13	14-24c	6-22	13PR-52c
1-7	13I-23e	2-20	14-47a	4-2	2010B-6	5-14	15PR-1a	6-23	13I-60e
1-8	C*	2-21	15PR-49d	4-3	2011-6	5-15	14-37b	6-24	13PR22d
1-9	B*	2-22	13-42c	4-4	2009B-2	5-16	15PR-6c	6-25	15PR-25b
1-10	B*	3-1	12I-2	4-5	2013I-3	5-17	15PR-14a	6-26	14-19c
1-11	13I-57e	3-2	2015PR-1	4-6	15Pr-17c	6-1	2015PR-7	6-27	14-29b
1-12	14-3d	3-3	2013I-2	4-7	13I-32e	6-2	2010B-1	6-28	14-20d
1-13	15PR-31d	3-4	2010B-2	4-8	13I-51b	6-3	2009B-1	6-29	14-22b
2-1	2015PR-4	3-5	2013I-5	4-9	13I-61e	6-4	2011B-6	6-30	14-23b
2-2	2013PR-7	3-6	2012-2	4-10	13I-62d	6-5	2010-1	6-31	14-38b
2-3	2010-5	3-7	2013-5	4-11	13I-67b	6-6	2015PR-5	6-32	13-14a
2-4	2011B-6	3-8	13I-1e	4-12	15PR-42b	6-7	2011B-1	7-1	2010-2
2-5	2011-5	3-9	13I-8b	4-13	13PR-53a	6-8	2011-1	7-2	2011B-5
2-6	15PR-2c	3-10	13I-9e	4-14	15PR-43b	6-9	2012I-1	7-3	2012-6
2-7	13I-4a	3-11	13I-21d	5-1	2015PR-3	6-10	2012-1	7-4	2011-2
2-8	13I-5c	3-12	13-25d	5-2	2012I-3	6-11	2013I-1	7-5	1992-7
2-9	13I-6c	3-13	13I-41b	5-3	2009B-5	6-12	2015PR-2	7-6	1997-9
2-10	13I-7b	3-14	13I-44d	5-4	2013I-2	6-13	15PR-10d	7-7	13I-33d
2-11	13I-42e	3-15	13I-53c	5-5	2012-3	6-14	15PR-13a	7-8	13I-38e
2-12	13I-47c	3-16	13I-63d	5-6	13I-29e	6-15	15PR-15d	7-9	13I-48a
2-13	13I-49d	3-17	13I-69b	5-7	13I-37b	6-16	15PR-16b	7-10	13I-65a

*not from a previous AP test.

Note: Unless otherwise notated, the multiple choice questions are from the 2013 International version (13I), modified and released in the fall of 2013. The remainder of the multiple choice comes from the released practice exam (13PR MC). I gave this exam to students as practice right before the review session. These questions I added were missed by more than ½ of my students who took the practice exam. In S 2015 additional most missed questions were added from the 2014 released MC exam.

The free response questions include: 1) Questions from the released practice exam(2013PR) 2) Questions from many other tests were added to supplement the concepts covered in the big ideas.

12I released 2012 international exam

Concepts - ATOMIC THEORY, BONDING, AND PERIODIC TRENDS

1. Electron configurations, Hund's rule, Pauli Exclusion principle, Heisenberg uncertainty principle, orbital diagrams, wave behavior and photons (c=□v, E=hv)
2 Trends of the periodic table a) size for atoms and ions b) size of ions c) IE, EA, EN
3. Effective nuclear charge (Z_{eff}) increases as more protons added to same energy level
Z_{eff} is a comparison tool. Coulomb's Law $F=kqq/d^2$
4. Effective nuclear charge (Z_{eff}) decreases as more shielding electrons are present.
5. When students talk about EN differences they are talking about bonds (within a molecule), you need to talk about IMF (between molecules)
6. Students often talk about atoms "wanting to gain/lose electrons", being happy, full, etc. Instead you need to refer to Coulomb's law (attraction of positive and negative), distance from the nucleus, shielding effect.
7. Correct use of spectroscopy (UV, PES, IR, VIS,). What is appropriate for what you are looking for? Electron transitions (probing electronic structure), molecular vibrations (bond type),
8. Vocabulary: IE (ionization energy), EN (electronegativity), EA (electron affinity), core electrons, valence electrons, shells (or energy levels), atomic and ionic radii,

Concepts - BONDING, LEWIS STRUCTURES, AND INTERMOLECULAR FORCES

1. Ionic bonds (ion-ion forces), metallic bonds (sea of electrons),
2. Covalent bonds, Lewis structures, geometric shapes, bond polarity, molecular polarity, resonance, hybridization, London dispersion forces (LDF), inter vs. intramolecular forces
3. Intermolecular Forces (IMF) are between molecules and help explain differences in FP, BP, solids, liquids, gases, and solubilities

a. ion-dipole (water and ionic compounds)
b. dipole – dipole with H bonding
c. dipole – dipole
d. London dispersion forces (LDF)

4. Molecular polarity depends on bond polarity **and shape** of the molecule
5. Property differences associated with different types of bonding
6. Solution formation and bond energy
1. Physical and chemical changes, oxidation / reduction – balancing equations
2. galvanic cells – { Red Cat}, cell potential, direction of current,
3. electrolytic cells- selection of electrodes
4. current, charge, Faradays, (voltage / EMF) (amps, coulombs and volts)
5. cell notation
6. salt bridge – "*balance of charge*" not electron balance,
Good salt bridge materials are soluble salts, not easily oxidized or reduced, doesn't interfere with given redox reaction, ie complex ion formation or precipitation
7. E^o and thermodynamically favored
8. $\Delta G^o = - n F E^o$
9. $E = E^o – (0.059 / n) \log K_c$
10. I = Q/t amps = coulombs/sec, Faraday = 1 mole of electrons = 96485C
10. Vocabulary –Anode, Cathode, Galvanic, Voltaic

Concepts – BALANCED EQUATIONS, STOICHIOMETRY, IONIC AND NET IONIC EQUATIONS, ELECTROCHEMISTRY

CONCENTRATION UNITS OF SOLUTIONS / COLLIGATIVE PROPERTIES (conceptual only)

1. Molarity M = mole of solute/ L of solution
2. mole fraction = x_a = mole of a /total moles in solution
3. Vapor Pressure Solution = ($x_{solvent}$) VP $_{pure\ solvent}$

Concepts List – KINETICS, REACTION MECHANISMS, COLLISION THEORY

1. Rate definition
2. Factors affecting rate
   a. [C]
   b. ΔT
   c. catalysis
   d. surface area
   e. nature of reactants – distinguish between homo- and heterogenous
      i. solids ii. Liquids iii. gases iv. Ions (solutions)
3. Collision theory – orientation and energy
4. Mechanism – relationship between ΔT, ΔS, ΔH – catalysis

5. Orders Rate Law – differential versus integrated
   a. determined by
      i. experimental comparison (20% or less)
      ii. graphing (80% or more)
   b. zero, first, second – determining % remaining and/or % reacted
      ex. $\text{Ln}\ (x_2/x_1) = kt$
6. Rate constants with units (units change with reaction order)
   a. unsuccessful versus effective collisions
   b. orientation and energy
7. Mechanisms are consistent if:
   - steps add up to balanced equation
   - slow step of mechanism will define the mechanistic rate law and rate law expression
   - no reaction intermediates in final rate law expression for comparison with the experimental rate law expression

Concepts – THERMODYNAMICS

1. $\Delta H^0{}_{rxn} = \sum \Delta H_f{}^0$Products - $\sum \Delta H_f{}^0$ Reactants
   $= \sum$ Bond Energy Reactants - $\sum$ Bond energy Products
   ΔH_{rxn} - exothermic **ΔH_{rxn} + endothermic**
2. $\Delta S^0{}_{rxn} = \sum S_f{}^0$ Products - $\sum S_f{}^0$ Reactants
   $\Delta S^0{}_{rxn}$ - ordered **$\Delta S^0{}_{rxn}$ + disordered**
3. $\Delta G^0{}_{rxn} = \Delta H^0{}_{rxn} - T\,\Delta S^0{}_{rxn}$
   $\Delta G^0{}_{rxn}$ -- thermodynamically favored
   $\Delta G^0{}_{rxn}$ + thermodynamically unfavored
4. $\Delta G^0{}_{rxn} = -RT \ln Q$ $Q = K_{eq}$ free energy and equilibrium R=8.31J/K*mol
5. $\Delta G^0{}_{rxn} = -nF\,E^0$ free energy and electrochemistry
   F = 96,500 coulombs / mole electrons
   Faraday's constant
6. Phase diagrams ?
7. $\Delta H_{rxn} = q = m\ (c)\ (\Delta T)$

Concept List – EQUILIBRIUM

All Problems are equilibrium problems because even if there are driving forces (ppt formation, gases, water formation) there is generally some aspect of the reaction that can be made to go backwards (unless the product becomes unavailable).

All problems involve stoichiometry: soluble salts, strong acids, strong bases
Some problems involve equilibrium: "insoluble" salts, weak acids, weak bases

For chemical reactions – K_{eq}, K_c, and K_p are the important quantities

For physical changes – K_a, K_b, K_{sp}, K_{ionize}, and $K_{dissocation}$ are the important quantities

Important points:

1. Law of mass action
   $aA + bB + \ldots \rightarrow rR + sS + \ldots$
   $K_c = [R]^r [S]^s \ldots / [A]^a [B]^b \ldots$
2. K_c for molarity for ions and gases
3. K_p with atm
   Relationship / connection between these $K_p = K_c (RT)^{\Delta n}$
4. Orientation of collisions
5. Shifting equilibrium – Le Chatlier's Principle
   a. solid
   b. liquid
   c. catalyst
   d. inert gas added

e. temperature changes (increasing T favors endothermic processes)
f. pressure / volume changes

6. Important vocabulary
   Driving force
   Favors (reactants or products)
   Shifts (in LeChatelier arguments)
7. $K > 1$ products favored
   $K < 1$ reactants favored
8. Excluded: solids, pure liquids, water (in aq solution) eg. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ K =[CO_2] or K_p=p CO_2
9. Typical question: Given K_c and the starting concentration of reactants, find the concentration (or pH) of products at equilibrium.
   Example: K_c of acetic acid = 1.754×10^{-5}. Find the pH of a 0.100 *M* solution of acetic acid.
10. Equilibrium constant for a reverse reaction = 1 / K of the value of the forward reaction.
11. When combining equations (using "Hess's Law"): $K_{overall} = K_1 \times K_2$
12. If out of equilibrium: Calculate the reaction quotient (Q) in a similar fashion to the way an equilibrium constant would be found. If:
    $K > Q$ forward reaction occurs to reach equilibrium
    $K < Q$ reverse reaction occurs to reach equilibrium
13. Problem solving: Learn when to make an approximation (needed for multiple choice and free response questions!). 5% rules usually works when value of K is 10^{-2} or smaller than value of known concentrations.
    Example: $A \rightarrow B + C$ $K = 3.0 \times 10^{-6}$

    If [A] = 5.0 M; find [C] at equilibrium

Concept List – <u>ACID – BASE</u>

pH = - log [H^+] pOH = - log [OH^-] $K_w = [H^+][OH^-] = 1 \times 10^{-14}$ at 25 ºC pKa + pKb = 14, pH + pOH =14

Definitions

Acid	Base	Theory

Donates H^+	Donates OH^-	Arrhenius
Donates protons	Accepts protons - {anions?}	Bronsted – Lowry

Conjugate Acid – Base Pairs

1. $HCl + H_2O \rightarrow H_3O^+ + Cl^-$
2. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
3. $HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$
4. $CO_3^{2-} + H_3O^+ \rightarrow HCO_3^- + H_2O$

A. K_a Weak Acid HCN → $H^+ + CN^-$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = 6.2 \times 10^{-10}$$

What is the pH of a 0.5 *M* HCN solution?

B. K_b Weak base $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

What is the pH of a 0.5 *M* NH_2OH solution?

C. K_{sp} Insoluble Salts $MgF_2(s) \rightarrow Mg^{2+} + 2F^-$ $K_{sp} = [Mg^{2+}] [F^-]^2 = 6.6 \times 10^{-9}$
What is the solubility of MgF_2 in molarity?

D. **Buffers** – a weak acid/base and its soluble salt (conjugate base or acid) mixture

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

What is the pH of a 0.5 *M* $HC_2H_3O_2$ in 2 *M* $NaC_2H_3O_2$ solution? $K_a = 1.8 \times 10^{-5}$

E. Salts of Weak Acids and Weak Bases
Ex.What is the pH of a 1 *M* $NaC_2H_3O_2$ solution?

Titrations and Endpoints
At endpoint: acid moles = base moles or $[H^+] = [OH^-]$ no matter the concentration or strength of Acid or bases
Strong acid – strong base endpoint pH = 7
Strong acid – weak base endpoint pH < 7
Weak acid – strong base endpoint pH > 7

The last two are important because of conjugate acid and base pairs

11. Acid strength – know the 7 strong acids: HCl, HBr, HI, HNO_3, $HClO_4$, $HClO_3$ and H_2SO_4 (removal of the first H^+ only)

a) binary acids – acid strength increased with increasing size and electronegativity of the "other element". (NOTE: Size predominates over electronegativity in determining acid strength.)
Example: $H_2Te > H_2O$ and $HF > NH_3$

b) oxoacids – Acid strength increases with increasing:
1) electronegativity
2) number of bonded oxygen atoms
3) oxidation state

of the "central atom". However, need to show as electron withdrawing groups rather than trends (trends need to be explained as a result of chemical principles rather than solely as a trend)
Example: $HClO_4$ $[O_3Cl(OH)]$ is very acidic

NaOH is very basic

Acid strength also increases with DECREASING radii of the "central atom"

Example: HOCl (bond between Cl and OH is covalent – acidic)
HOI (bond between I and OH is ionic – basic)

12. Acid Ionization Constant (K_a):

$HA + H_2O \rightarrow H_3O^+ + A^-$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

Example: $HF + H_2O \rightarrow H_3O^+ + F^-$

$$K_a = \frac{[F^-][H_3O^+]}{[HF]}$$

What is the pH of 0.5 *M* HCN solution for which $K_a = 6.2 \times 10^{-10}$?

13. Base Ionization Constant (K_b):

$B + H_2O \rightarrow BH^+ + OH^-$

$$K_b = \frac{[BH^-][OH^-]}{[B]}$$

Example: $F^- + H_2O \rightarrow HF + OH^-$

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

What is the pH of a 0.5 *M* NH_2OH solution for which $K_b = 6.6 \times 10^{-9}$?

Do equal number of K_a and K_b problems as they are equally likely!

14. **$K_a \times K_b = K_w = 10^{-14}$ for conjugate acid/base pairs @ 25 ºC!**

15. Percent ionization = $[H^+]_{equilibrium} / [HA]_{initial} \times 100$

16. **Buffers:**
Similar concentrations of a weak acid and its conjugate base -or-
Similar concentrations of a weak base and its conjugate acid
If these concentrations are large in comparison to SMALL amounts of added acid or base, equilibrium will be shifted slightly and the pH change resisted. Consider:

$HA \rightarrow H^+ + A^-$ $B + H_2O \rightarrow HB^+ + OH^-$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

$[H^+] = K_a [HA] / [A^-]$ $pH = pK_a + \log [A^-] / [HA]$ (Henderson-Hasselbach equation)

What is the pH of a solution which is 0.5 *M* $HC_2H_3O_2$ in 2 *M* $NaC_2H_3O_2$ for which $K_a = 1.8 \times 10^{-5}$?

17. Polyprotic Acids: H_3PO_4, H_2SO_4, $H_2C_2O_4$, etc.
18. Equivalence Point – the point at which stoichiometric amounts of reactants have reacted.

NOTE: This only occurs at pH = 7 for the reaction of a strong acid with a strong base. The equivalence point will occur ABOVE pH = 7 (more basic) for a weak acid / strong base titration. (the conjugate base of the weak acid will react with water.) The equivalence point will occur BELOW pH = 7 for a weak base / strong acid titration (the conjugate acid of the weak base with react with water).

19. Indicators – select bases on the pH at the equivalence point.

20. **Titration curves:**

a) Weak acid / strong base $HA + OH^- \rightarrow A^- + H_2O$

NOTE: Graph should have "pH" as the vertical axis and "added base" as the horizontal axis. The graph should be in an "S" shape. The middle of the lower part of the "S" indicates the point of maximum buffering where [HA] / [A$^-$] = 1. The middle of the "S" is the equivalence point (above pH = 7) and [HA] = 0. The top part of the "S" levels off at the pH of the base solution. At the ½ titration point, the pH=pKa.

b) Weak base / strong acid $B + H_3O^+ \rightarrow BH^+ + H_2O$

NOTE: Graph should have "pH" as the vertical axis and "added acid" as the horizontal axis. The graph should be in a "backwards S" shape. The middle of the upper part of the "backwards S" indicates the point of maximum buffering where [B] / [HB$^+$] = 1. The middle of the "backwards S" is the equivalence point (below pH = 7) and [B] = 0. The bottom part of the "backwards S" levels off at the pH of the acid solution. At the ½ titration point, the pH = pKa and the Kb can be found from the Ka value.

c) Weak diprotic acid / strong base $H_2A + OH^- \rightarrow HA^- + H_2O$

$HA^- + OH^- \rightarrow A^{2-} + H_2O$

NOTE: Graph should have "pH" as the vertical axis and "added base" as the horizontal axis. The graph should be in a "double S" shape. The middle of the lower part of the "first S" indicates the point of maximum buffering of the first buffering zone where [H_2A] / [HA^-] = 1. The middle of the "first S" is the first equivalence point where [H_2A] = 0. The top of the "first S" (i.e. the lower part of the "second S") indicates the point of maximum buffering of the second buffering zone where [HA^-] / [A^{2-}] = 1. The middle of the "second S" is the second equivalence point where [HA^-] = 0. The top part of the "second S" levels off at the pH of the base solution. At the ½ titration points, the pH = pKa.

21. **Solubility Product (K_{sp})**

Example 1: $Co(OH)_2(s) \rightleftharpoons Co^{2+} + 2OH^-$ $K_{sp} = [Co^{2+}][OH^-]^2$

(don't forget – molar concentration of OH^- is twice the solubility)

Example 2: Solubility of Ag_2SO_4 is 0.016 mol L^{-1} (5.0 g L^{-1}). Find the K_{sp} of Ag_2SO_4. (Answer: $K_{sp} = 1.5 \times 10^{-5}$)

22. **Ion product (Q_i) – equivalent to the "reaction quotient"**

$K_{sp} > Q_i$ all ions in solution; more solid will dissolve

$Q_i = K_{sp}$ equilibrium – solution is saturated

$K_{sp} < Q_i$ precipitation will occur until $Q_i = K_{sp}$